GASEOUS EMISSIONS FROM HERDING AGENT-MEDIATED IN-SITU BURNING FOR ARCTIC OIL SPILLS

By

Patrik Pettersson Sartz

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APPROVED:

Dr. Srijan Aggarwal, Committee Chair
Dr. David Barnes, Committee Member
Dr. William Schnabel, Committee Member
Dr. Leroy Hulsey, Chair
Department of Civil and Environmental Engineering
Dr. Douglas Goering, Dean
College of Engineering and Mines
Dr. Michael Castelini, *Dean of the Graduate School*

Abstract

If a crude oil spill were to occur in partially ice-covered waters, many of the response tactics typically utilized in either open water or completely ice-covered conditions would become inefficient. In such situations, in-situ burning (ISB) can prove to be an efficient response tool; herding agent application is one available approach to thicken an oil slick. This study assessed the impacts on air quality following ISB tests on crude oil, in combination with herding agents, in partially ice-infested waters. The research focused on measuring downwind concentrations of respirable particulate matter ($PM_{2.5}$) and seven different combustion gasses (CO, CO_2, NO, NO_2, NOx, SO_2, and VOCs) during five ISB events, with sampling instruments placed in-plume and 6-12 m away from the source area. The study also investigated if the utilized herding agent was detectable in the airborne plume. Findings include:

1) Concentrations of particulate matter (<2.5μm in diameter), SO_2, and CO were found to significantly ($P < 0.01$) exceed various exposure limits and air quality standards, while the remaining compounds measured were significantly ($P < 0.01$) below established exposure limits. Also, downwind, in the smoke plume, measured concentrations of SO_2, NO_x, and total VOCs were higher than found in previous studies. It should be noted that instrument and methods not specifically approved by the U.S. Environmental Protection Agency, Occupational Safety and Health Administration, and the National Institute for Occupational Safety and Health were utilized during this study;

2) GC/MS analysis of aerosol samples collected utilizing a flow meter and carbon sorbent tubes in the smoke plume; the Siltech OP-40 silicone based functional group of the applied herding agent was not detected in the collected samples analyzed using GC/MS.

Future research should include additional scalability studies where the concentrations of

particulate matter and various combustion gasses are compared to modeled concentrations using computer software. Additional research is also needed to find a cost-effective method to decrease the amount of particulate matter during an in-situ burn. It is also recommended that guidance specific for conducting in-situ burns of crude oil or refined petroleum products in the Arctic is written and published by regulatory agencies, so the industry can rapidly make plans and propose such tactics if an incident did occur where mechanical or other non-mechanical response tactics are not feasible.

Dedication

I dedicate my thesis work to my family and many friends. A special feeling of gratitude to my loving wife, Annie, whose words of encouragement and push for tenacity ring in my ears.

I also dedicate this thesis to my many friends and work family who have supported me throughout the process. I will always appreciate all they have done, especially Ashley Adamczak for helping me develop my constructive thinking skills, Kelley Tu for the many hours of proofreading, and Jessica Starsman for guiding me through the darker moments of graduate school.

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1 Introduction

1.1 Overview

With increased vessel traffic through the Northwest Passage carrying crude oil and other bulk fuels such as No. 2 fuel oils and Bunker C, as well as the potential for continued exploration and production in the Chukchi and the Beaufort Sea, the risk of a crude oil spill has increased. If a spill were to occur in ice-covered waters of the Arctic, most of the oil spill response approaches normally utilized in either open water or completely ice-covered conditions become impractical because containment is not an option, making available mechanical recovery options less efficient (Arctic Response Technology, 2015). Non-mechanical response approaches such as in-situ burning (ISB) can remove 90-98% of the initial amount of spilled oil (API, 2004; Buist et al., 2013a). Oil removal efficiency is increased if the oil slick is contained by a barrier, such as ice because the slick thickness is enhanced (Buist et al., 2013a), which promotes ignition and sustained burning required for an effective ISB operation.

To aid effectiveness during an ISB by reaching an optimal slick thickness of 6 mm, surfactants or herding agents have been developed and experimented with since the early 1970s. The herding agents act by spreading over the water surface, forming a monomolecular layer; due to their higher spreading pressures compared to most crude oils (mid-40 mN/m vs. 10-20 mN/m, respectively), they continue to contract and thicken the oil slick until attaining equilibrium (Buist et al., 2013a). Also noted by Buist et al. (2013a), herding agents work in both open water (if applied around the entire perimeter of an oil slick) and in light pack ice conditions. There are currently two products authorized by the United States Environmental Protection Agency (EPA) and listed in the National Contingency Plan Product Schedule for use as herding agents on oil discharges: Siltech OP-40 and Thickslick 6535. Siltech OP-40 is silicone based, while Thickslick

6535 is hydrocarbon based. Both have been proven to "work in all water temperatures and salinities and works best with fluid petroleum that has not weathered significantly" (USEPA, 2015a; USEPA, 2015b).

One of the major considerations when choosing in-situ burning as an oil spill response measure is any potential impacts to downwind air quality. Several previous studies have addressed this issue and found that the particulate matter or soot produced is the main compound of concern (Fingas, 2013). Fingas (2013) also notes that particulate matter will precipitate with distance/time away from the combustion site, and therefore does not pose a threat to humans or wildlife past approximately ½ km unless there is an inversion. In addition, another study published by Fingas (2014a) states that current knowledge regarding crude oil in-situ burns allows for stakeholders to provide predictions for emission levels and to determine safe distances. The same study concluded that a standard crude oil fire would not exceed exposure limits for emissions beyond 1km.

1.2 Study Hypothesis and Objectives

This study focused on the atmospheric emissions during an ISB event, and if the concentrations observed downwind in the smoke plume could pose an imminent and substantial threat to human health and safety. Specifically, the objective of this study was to measure downwind, in the smoke plume, concentrations of atmospheric particulate matter and various combustion gases [Carbon Dioxide (CO), Carbon Dioxide (CO_2), Nitric Oxide (NO), Nitrogen Dioxide (NO_2), Nitrogen Oxides (NOx), Sulfur Dioxide (SO_2), Volatile Organic Compounds (VOCs)] as well as comparing the data to established exposure limits, air quality standards, and previous studies. Furthermore, one additional objective was to investigate potential presence of

any volatilized herding agent functional groups within the smoke plume.

We hypothesized that:

- By using instruments more easily movable, measurements from within the smoke plume could be collected with higher concentrations than previous studies.
- When comparing logged data to wind speed during burns, we would see decreased incomplete combustion with increased wind speed, and therefore decreased concentrations of particulate matter as well as CO, NO, NO_2, NO_x, SO_2, and VOCs.
- There would be no presence of volatilized herding agent functional groups, due to the high temperature needed for volatilization and inadequate heat transfer from flames to the water-oil interface where the herding agent would be present.

Compounds to measure were selected based on several previous studies, including Fingas (2014a), which measured particulate matter, Polycyclic Aromatic Hydrocarbons (PAHs), VOCs, dioxins, dibenzofurans, carbonyls, CO, CO_2, SO_2, and several other compounds during more than 50 crude oil and diesel burns. Additionally, in their report "In Situ Burning in Ice-Affected Waters: A Technology Summary and Lessons Learned from Key Experiments," Buist et al. (2013a) states that the seven main components of a smoke plume from an in-situ burn include CO, CO_2, SO_2, smoke particulates, VOCs, PAHs, and NO_x. Ross et al. (1996) concluded that the primary combustion products of crude oil are CO_2, water, and particulate matter, as well as other gaseous pollutants such as CO, NO_x, SO_2, and a wide range of organic compounds such as VOCs and PAHs. The reader should note that this study did not utilize instruments or sampling methods established and approved by either Occupational Safety and Health Administration (OSHA), the National Institute for Occupational Safety and Health (NIOSH), or the U.S. Environmental

Protection Agency (EPA), but instead smaller-sized handheld instruments that are easily transported to and utilized in the field.

1.3 Commonly Used Response Tactics, and Their Lack of Practicability in the Arctic

Historically, regulating agencies such as the U.S. Coast Guard, U.S. Environmental Protection Agency, U.S. Fish & Wildlife Service, and Bureau of Safety and Environmental Enforcement have considered mechanical response tactics, which remove the contaminant out of the environment in an unaltered state, be the primary method for releases into the marine environment, and that non-mechanical tactics only be used if they have shown to equate in a net environmental benefit. In Alaska, the Alaska Department of Environmental Conservation (ADEC; 2006) has stated that "mechanical response methods are the primary and preferred techniques for responding to an oil spill" (pg. B-III-i). The main reason for this is that many non-mechanical response tactics, such as the use of dispersants or in-situ burning, to some extent, only alter the shape or composition of the contaminant, which can then pose a threat to the ecosystem in the affected area. Dispersants cause the oil to convert into micron-sized droplets (<100 μm in diameter) that disperse throughout the water column. When burned, the ignited oil is also removed from the water surface and dispersed through the atmosphere as carbon dioxide (CO_2) and water (H_2O) when the oxygen supply is sufficient and complete combustion occurs.

If a release occurs in a marine environment, response tactics are also often classified as either offshore, near-shore or onshore. Mechanical off-shore tactics mainly consist of deploying containment boom and conducting recovery tactics using various skimming devices, while mechanical near-shore tactics include all of the off-shore tactics but also other booming techniques such as diversion, deflection, and exclusion booming. On-shore mechanical tactics

include an array of other recovery methods, with everything from flush-and-suck to the use of hand tools for removal of contaminated vegetation. Near-shore or on-shore tactics are never preferable because the released product has then migrated from on type of environment, the marine, into another, the terrestrial, with the potential to affect the soil, vegetation, wildlife, structures, and cultural sites present there. Therefore, off-shore tactics, whether mechanical or non-mechanical, are always preferable if practicable.

Fortunately, the Arctic has never experienced a major oil release, but cleanup would, without any doubt, prove challenging if one was to occur. Ice coverage ranging from 30-to-70% will prevent many of the mechanical response tactics from being utilized, especially those requiring booming. The Arctic also lacks what many other offshore lease areas have readily available: vessels of opportunity and logistical support (Arctic Response Technology, 2015). Any responsible party causing a release in the Arctic would have to provide the majority of the response resources themselves, without being able to rely on local fishing or transportation vessels being available for rent or hire. The Arctic also lacks an adequate amount of land-based facilities to support a large-scale mechanical response effort, which requires more resources, i.e., food, fuel, lodging, landing areas for fixed-wing aircraft and helicopters, port facilities for deep-draft vessels, mechanical support, facilities for interim storage of waste (Arctic Response Technology, 2015), than a non-mechanical response effort. Furthermore, the U.S. and Canadian lease areas, where oil exploration and production would occur, are located at least 100 miles away from the shoreline, which would increase travel times for vessels conducting recovery operations and further reduce the effectiveness of a mechanical response (Arctic Response Technology, 2015). Off-shore response tactics, using only mechanical devices, would no longer

be a feasible option in that scenario. Regulatory agencies must start considering non-mechanical options, such as dispersant and in-situ burning, as a primary response tactic.

1.4 Non-Mechanical Tactics for an Off-Shore Response

Dispersants and in-situ burning are tools that have always been available during a major response but have only been utilized on rare occasions. However, during the Deepwater Horizon (DWH) incident in 2009, both tactics were utilized heavily and gained some trust from both the regulatory and response community. The final report from the DWH showed that an estimated 1.6 million barrels (69.1 million gallons) of crude oil, of the 4.9 million barrels (205.8 million gallons) released, were recovered during the response effort, with 16.5% removed by in-situ burns and 23.9% through the use of chemical dispersants (Gullett et al., 2017).

Dispersants, such as Corexit 9500, were developed in the late 1970s. They work by changing the structure of the oil slick to break it apart into smaller globules, which can then sink and disperse throughout the water column. Breaking the oil slick apart into smaller fragments increases the surface area, and the oil becomes more readily biodegradable by the existing microbial community. The act of dispersing the oil also removes the risk of the product threatening present habitats or the species that inhabit them through smothering. However, oil dispersed through the water column increases the amount of oil in an area in the short term, which can cause temporary impacts to sensitive marine species (Arctic Response Technology, 2015). Previous studies have therefore concluded that dispersants should not be used close to sensitive sub-surface resources, such as coral reefs and known spawning beds, and should be used with caution in shallow waters (defined as less than 10 m in depth or within 3 km offshore; Potter et al., 2012). Some concern has been raised regarding the potential toxicity of dispersants themselves, as well as the fact that it is harder to track the oil's fate once it is dispersed

throughout the water column (Arctic Response Technology, 2015). Also, to be effective, dispersants require a certain amount of mixing energy, e.g. through normal wave action, which might be insufficient in the Arctic, where the oceans remain partially ice-covered for long periods of time (Potter et al., 2012).

In-situ burning, in conjunction with various other resources such as fire-resistant boom, herding agents, or natural containment, has been successfully utilized as a response tactic since the late 1960s, both onshore and offshore (Potter et al., 2012). Of special interest has been the potential to utilize chemical herding agents, surfactants with higher spreading pressure than crude oil, to contract and thicken oil slicks for higher burn efficiency when planning for a response in the Arctic during medium (30-to-70%) ice concentrations (Potter et al., 2012). Data collected as part of research studies, as well as during actual spill events, have shown oil removal rates from 42% up to 99% (API, 2004; Buist et al., 2013b; L. van Gelderen et al., 2016). In the Arctic, in-situ burning should be considered a primary response tactic, because it is a viable option in most, if not all, ice conditions (Potter et al., 2012), requires few resources to implement, and can be conducted while minimizing the number of responders placed in harm's way through the utilization of helitorches and Unmanned Aerial Vehicles (UAVs). Besides the potential physical hazard from the flames themselves, the primary concern when burning crude oil is the creation of hazardous byproducts, such as particulate matter and various combustion gasses when the oxygen supply is insufficient and incomplete combustion occurs (Potter et al., 2012; Fingas, 2014b). In-situ burning also leaves behind a residue that can sink and smother plants and benthic species if the burned oil has an initial density greater than 0.865 g/cm^3 (NOAA, 2017). The residues have, however, been shown to not have acute toxicity to key indicator species living in salt- or freshwater (Potter et al., 2012).

1.5 In-Situ Burning in Conjunction with Herding Agents

To aid effectiveness during an ISB by reaching an optimal slick thickness of 6 mm, surfactants or herding agents have been developed and experimented with since the early 1970's. The herding agents act by spreading over the water surface into a monomolecular layer, and due to their higher spreading pressures compared to most crude oils (mid-40 mN/m vs. 10-20 mN/m, respectively), they continue to contract the oil thicker slicks until equilibrium (Buist et al. 2013a). Slicks under the influence of herding agents have been shown to reach thicknesses of 3-8 mm (Ross, 2007). Also noted by Buist et al. (2013a), herding agents work in both open water (if applied around the entire perimeter of an oil slick) and in light pack ice conditions. There are currently two products authorized by the United States Environmental Protection Agency (EPA) and listed in the National Contingency Plan Product Schedule, for use on oil discharges: Siltech OP-40 and Thickslick 6535. Siltech OP-40 is silicone based, while Thickslick 6535 is hydrocarbon based herding agent. Both have been proven to "work in all water temperatures and salinities and works best with fluid petroleum that has not weathered significantly" (USEPA, 2015).

Several studies have been conducted in recent years to determine the effectiveness of herding agents in various percentages of ice coverage and scale of experiments. L. van Gelderen et al. (2016) found that burning efficiency was 42-to-86% during small-scale experiments and 42-to-68% during meso/intermediate-scale experiments, both with 30-to-70% ice coverage. Bullock et. al. (2017) measured average burn efficiencies of 38%, 64%, and 79% for small/bench scale experiments, meso/intermediate-scale experiments, and field-scale experiments, respectively, with ice coverage ranging from 6% up to 70%. Issues noticed during studies utilizing herding agents in conjunction with in-situ burning include fracturing of oil when herded

(Ross, 2007; L. van Gelderen et al., 2016), which makes ignition of all viable slicks difficult or impossible. There could be several reasons for the fracturing mechanism, including ice present on the water surface (Ross, 2012) or an interrupted application of the herding agent. Bullock et al. (2017) also noted that burn efficiency decreased if herder volume was increased significantly above the manufacturer's recommended application rate. Another study found that herders were effective at reducing slicks to burnable areas in pack ice when conditions are calm, but that a wind speed of more than 1.5 m/s may be sufficient to reduce the effect completely (Fingas, 2014a).

With any type of in-situ burning of crude oil comes the potential for emissions that could potentially be hazardous if inhaled by responders, members of the general public, or wildlife. According to Fingas (2014b), if weather conditions (e.g. presence or absence of inversion, or wind direction at higher elevations) are unknown, burning should not be carried out within 4km of heavily populated areas. If conditions are known and favorable, burns can be carried out closer, but it is recommended that an attempt is made to evacuate residents living close to the burn site (Fingas, 2014b). Evans et al. (2001) calculated smoke yield specific to Alaska North Slope (ANS) crude oil and found that, due to its higher smoke yield, particulate matter concentrations could remain above 35 $\mu g/m^3$ (the allowable 24-hour average concentration per the National Ambient Air Quality Standard) up to 5 km from the burn site.

In terms of potential harm to wildlife due to emissions, Fingas (2014b) stated that "wildlife on land is generally not affected if burning is conducted more than 1km away from shore or sensitive areas. It has also been observed that birds will avoid the burning site and therefore are unlikely to be affected. Similarly, marine species should not be affected as the water column normally does not become contaminated." That finding was echoed by ASTM

(2003), who also stated that in-situ burning does not release combustion by-products to the water column. Strand and Andren (1980) did, however, conclude that both aromatic and polyaromatic hydrocarbons (PAHs), created by combustion processes other than from in-situ burning of crude oil, will accumulate in the surface microlayer (the upper 1 mm of the water column) until removed by absorption or sedimentation. They also noted that the PAH compounds have been linked to tumors and possibly reproductive disorders in marine fish (Strand & Andren, 1980). The Endangered Species Act (ESA) Memorandum of Agreement (MOA) does state that U.S. Department of Commerce-National Marine Fisheries Service and/or Department of Interior-Fish and Wildlife Service representatives will conduct an emergency consultation and provide the Federal State On-Scene Coordinator (FOSC) with recommendations when a threatened or endangered species and/or their critical habitat(s) are, or could be, present in the area affected by a proposed in-situ burn (ADEC et al., 2008). For both wildlife and humans, particulate matter or soot production has been found to be the main concern, but several potentially harmful combustion gasses are also formed during an ISB of crude oil.

1.6 Crude Oil Composition and the Compounds Emitted During an ISB

Crude oils are mixtures of hydrocarbon compounds ranging from smaller, volatile compounds to very large, non-volatile compounds (Fingas, 2012). Depending on in which geological formation the oil is found, the percentage of hydrocarbon compounds, categorized as saturates, olefins, aromatics, and polar, varies (Fingas, 2012). The group of saturates, consisting primarily of alkanes, are compounds of hydrogen and carbon that are connected solely by single bonds (Fingas, 2012). Olefins are hydrocarbon compounds that contain one or more carbon to carbon double bond, which makes them unsaturated (each double bond displaced four hydrogen atoms). The aromatics consist of hydrocarbons that have formed a ring structure, containing at

least six carbons with three double bonds (Fingas, 2012). The BTEX compounds (benzene, toluene, ethylbenzene, and the various xylene configurations) are the most common aromatic compounds and also known to be both volatile and a threat to human health due to their high toxicity (Fingas, 2012). Polyaromatic hydrocarbons (PAHs) are compounds consisting of at least two benzene rings. Polar compounds are those that have a higher polarity or reactivity due to bonding with compounds such as sulfur, nitrogen, or oxygen (Fingas, 2012). The smaller polar compounds are called resins (responsible for oil adhesion), while the larger are called asphaltenes. If the asphaltene content is high for a crude oil type, the oil has been found to have a higher density than water and therefore sink (Fingas, 2012). The crude oil produced within the various lease areas of the Alaska North Slope oil fields, the "Alaska North Slope (ANS) crude oil," has been found to have a sulfur content of 2.62%, with the remaining hydrocarbons consisting of 65.28%w/w saturates, 16.51%w/w aromatics, 14.72%w/w resins, and 3.49%w/w asphaltenes (Fingas, 2010b). In addition to hydrocarbons, compounds such as sulfur, nitrogen, oxygen, and sometimes mineral salts, as well as trace metals such as nickel, vanadium, and chromium are also found in crude oil (Fingas, 2012). Flagan and Seinfeld (1998) reported that crude oil contains 0.1-to-0.2% nitrogen on a mass basis and that some have levels as high as 0.5%.

During an ISB, complete combustion will occur if there is sufficient air supply and the hydrocarbons of the crude oil react with oxygen to form carbon dioxide (CO_2) and water (H_2O). Incomplete combustion (also called partial combustion) occurs when there is an insufficient amount of oxygen available (API, 2004). The hydrocarbons are still oxidized to water, but carbon monoxide (CO) is produced instead of CO_2. Incomplete combustion also leads to the production of black smoke, caused by the presence of large quantities of particulate matter of

various sizes (API, 2004). Once combustion has commenced, the ratio of in-situ burn end-products has been found to be 83-89% gasses (including water vapor), 9-15% particulate matter, 1-10% residue, and less than 1% water soluble fraction (API, 2004). The below sections describe how the particulate matter and various combustion gasses are created, as well as the potential health and environmental effects of each compound.

1.6.1 Carbon Dioxide (CO_2)

Carbon dioxide is formed during complete combustion when the hydrocarbons of the crude oil react with oxygen supplied by the ambient air to generate H_2O and CO_2. Although CO_2 can be toxic at high concentrations as well as an asphyxiant, levels around a burn site have been shown to be significantly below any health concerns (Fingas & Punt, 2000; API, 2004).

1.6.2 Carbon Monoxide

Carbon monoxide is formed during incomplete combustion when there is an insufficient amount of oxygen. Hydrocarbons in the crude oil react with oxygen but only form water and CO. Carbon monoxide is a highly toxic compound and due to its high affinity to hemoglobin, will replace the oxygen in the blood stream and cause hypoxia in cells of the body (Barnea, 1995). CO does not, according to Fingas (2014b), pose a threat because levels around or downwind of a burn site are well below any established exposure limits and often below instrument detection limits. Significant levels of CO have only been measured when the burn is inefficient, for example when water is sprayed onto the fire (Fingas, 2014b).

1.6.3 Particulate Matter or Soot (solid particles)

Particulates are formed during incomplete combustion, when elemental carbon particles and hydrocarbons initially contained in the crude oil rise with the heat of the burn, travel into the atmosphere (Mullin & Champ, 2003), and remain suspended long enough to potentially be inhaled (ADEC et al., 2008). Since these particulates absorb light to a high degree, the smoke plume is usually black (Barnea, 1995). Soot particulates often contain a number of adsorbed and absorbed chemicals, such as PAHs (Mullin & Champ, 2003). Particulate matter is categorized based on the size of the particle, and the three most commonly used categories are PM-1 (<1 μm), PM-2.5 (<2.5 μm), and PM-10 (<10 μm). Fingas et al. (1999) found that PM-10 concentrations were about 70 % of the total particulate concentration (TSP) and that PM-2.5 concentrations equate for around 50 % of the TSP.

The size of the particle must be taken into consideration when determining potential health effects, as it affects how far the particles travel before they settle out of the air and how deeply they are inhaled into the lungs (ADEC et al., 2008). Particulates 5-to-10 μm in diameter may be inhaled, but most are deposited in the upper respiratory tract and cleared by mucociliary action, which is efficient and relatively rapid (ADEC et al., 2008). Only particulates smaller than 5 μm in diameter reach the sensitive alveolar portion of the lungs (ADEC et al., 2008). Exposure to high levels of particulate matter [several milligrams (mg) of particulate per cubic meter (m^3) of air] can overwhelm the respiratory tract and cause breathing difficulties and has been linked to premature deaths, chronic bronchitis, and aggravated asthma (Barnea, 1995). Lower concentrations are still a concern, due to the fact that a 100 $\mu g/m^3$ increase in measured daily particulate level

has been found to be associated with a six percent increase in mortality (Barnea, 1995).

Several studies have investigated the effects of adding a smoke suppressant, such as products containing ferrocene or pumice stone, and found that 70-to-95 % of the soot or particulate matter production can be reduced (Buist et al., 1999; Demirel & Barsan, 2016). Ferrocene is a metallocene, a type of organometallic chemical compound consisting of two cyclopentadienyl rings bound on opposite sides of a central metal atom, which has been found to be insoluble in water and slightly soluble in hydrocarbons (Buist et al. 1999). Toxicity studies have shown that ferrocene is relatively nontoxic, and studies using the compound during in-situ burns have shown a 90-to-95% reduction in soot or particulate matter production when applying 2% ferrocene per total weight of oil to be burned (Buist et al., 1999). Unfortunately, ferrocene powder is expensive, has a higher density than water (causing it to sink if applied outside the oil slick), and due to the compound only being "slightly soluble in hydrocarbons," it takes a long time to dissolve in the crude oil before a burn can occur (Buist et al., 1999). However, various organic derivatives have been produced that are liquid at room temperature and more soluble in the oil compared to the powder form of ferrocene (Buist et al., 1999). The most promising hybrid is "RMS 9757" and has been shown to reduce soot or particulate matter production with 70% when applied at 0.5% per weight of oil to be burned (Buist et al. 1999).

Research related products that reduce particulate matter was shelved after RMS 9757 was invented in the late 1990's, mainly due to high costs of the end product. Demirel and Basan (2016) did, however, recently publish a study conducted to decrease soot product during an in-situ burn of crude oil using Ecopomex™, a product made by

pumice stone. Ecopomex™ is a hydrophobic and oleophilic product that has been shown to be able to float on water for more than four weeks and can absorb up to 35 % of its weight in hydrocarbons. The contained hydrocarbon/Ecopomex™ mix can then be recovered as is and burned ex-situ so the Ecopomex™ can be reused (up to 20 times), or burned in-situ. If burned in-situ, the study conducted by Demirel and Basan (2016) showed that soot production could be reduced up to 66%. Unfortunately, the study also found that burn efficiency was reduced when Ecopomex™ was applied. This can be contributed to the fact that the agent absorbs a certain amount of the oil that is not incinerated when in contact with water (Demirel & Basan, 2016). This percentage of the oil is therefore not removed from the water surface, although contained by the Ecopomex™, but would potentially need to be removed by mechanical means.

1.6.4 Sulfur Dioxide (SO_2)

Sulfur dioxide is formed when sulfur in the crude oil, often contained as hydrogen disulfide (H_2S), reacts with oxygen during a burn to form SO_2 and H_2O. The amount of SO_2 produced varies with the sulfur content of the crude oil. SO_2 is acutely toxic at high concentrations (>100 ppm) and causes breathing difficulties and airway obstructions in humans (ATSDR, 2014), but will irritate the eyes and respiratory tract even at lower concentrations when it reacts with water to form sulfuric acid on those moist surfaces (Barnea, 1995).

1.6.5 Oxides of nitrogen, NO & NO_2, and NO_x

Nitric oxide (NO) is formed both when atmospheric/molecular nitrogen and

oxygen, N_2 and O_2, react at temperatures above 1000°C, and when nitrogen contained in crude oil reacts with atmospheric O_2 (Flagan & Seinfeld, 1988) during an ISB. The last mechanism is the minor contributor of NO emissions from crude oil fires, as only 20-to-30% of the nitrogen contained is converted (Flagan & Seinfeld, 1988). NO, in its reactive or unstable form, then bonds with oxygen and is converted to nitrogen dioxide (NO_2) in the atmosphere. Both NO and NO_2 belong to the family of nitrogen oxides (NO_x; Flagan & Seinfeld, 1988).

NO, and NO_2 have been found to be strong irritants to the eyes and respiratory tract (ADEC et al., 2008), and short-term exposure to NO_2 may lead to issues with airway responsiveness and lung function for children, the elderly, and adults with existing respiratory illnesses (API, 2004). API (2004) also reports that "long-term exposure to NO_2 may lead to increased susceptibility to respiratory infection and may cause changes in the lungs" (pg. 36), mainly because of its low solubility, which increases the potential that the gas reaches deep portions of the lungs.

In terms of environmental impact, NO_2 has been found to react in the presence of air and ultraviolet light (UV) in sunlight to form ozone (O_3) and NO. The NO then reacts with free radicals in the atmosphere, which are also created by the UV acting on volatile organic compounds (VOCs). The free radicals then recycle NO to NO_2. Through that process, each molecule of NO can produce ozone multiple times. This cycle will continue up to five times until the VOCs are reduced to short chain carbon compounds that cease to be photoreactive. NO_x in the atmosphere is also captured by moisture to form acid rain, which, along with cloud and dry deposition, severely affects certain ecosystems (EPA, 1999).

1.6.6 Volatile Organic Carbons (VOCs)

VOCs, such as benzene, toluene, n-hexane, and naphthalene, have been found to readily evaporate during an in-situ burn and are also released naturally from oil slicks (Fingas, 2014b). VOCs have been found to cause acute health effects such as nausea and headaches at high concentrations (ADEC et al., 2008), and some VOCs are suspected carcinogens (API, 2004). Fingas and Punt (2000) found high concentrations of VOCs within 50-to-100 m from a burn site but also found that even higher levels (up to three times higher) are emitted from an unburned, evaporating, oil slick. Therefore, in-situ burning of crude has been found to lower air concentrations of VOCs even more so than any other remedial actions (ADEC et al., 2008).

1.6.7 Polycyclic Aromatic Hydrocarbons (PAHs)

PAHs are present in all crude oil, with concentrations varying from 1-to-0.001 %w/w (Mullin & Champ, 2003). Most of the PAH compounds are combusted and converted to fundamental gases during a burn, but due to their low vapor pressures and low flammability (compared to other compounds found in crude oil), some remain as part of the burn residue and some is adsorbed or absorbed to the emitted particulate matter (Barnea, 1995; API, 2004). Mullin and Champ (2003) also found that, compared to the original oil, the soot contained a similar concentration of some higher molecular weight PAHs and lower concentrations of lower molecular weight PAHs. This would be a concern because the higher molecular weight PAHs are generally more toxic. This is, however, offset by the fact that the overall concentration of PAHs in the soot and residue is much less than in the original oil.

Health concerns related to PAHs are due to the fact that some are classified as known or suspected carcinogens (ADEC et al., 2008). Westphal et al. (1994) estimated an excess cancer risk of 5 in 100,000 from breathing or ingesting PAHs in the soil after a hypothetical burn of 10,000 gallons of crude oil, which is still within USEPA's guidelines for acceptable risk levels. They did not find any non-carcinogenic effects caused by PAHs during a burn and therefore concluded that any potential health effects from the compounds should not influence the decision on whether or not to burn (Westphal et al., 1994).

1.6.8 Dibenzo-p-dioxins and Dibenzofurans (PCDD/PCDF)

PCDDs and PCDFs are often produced by burning chlorine-containing organic material, but the formation of these compounds requires that both organic carbon, oxygen, and chlorine is present (Heidelore, 2009). Several previous studies have analyzed particulates precipitated downwind, and residue produced from the burns for the presence of PCDD/PCDF but found that toxic compounds were at background levels at test fires, indicating no production by oil fires (Fingas, 2014b). Gullett et al. (2016) found, however, that particulate matter emitted during 27 in-situ burns conducted as part of the Deepwater Horizon response did contain PCDD/PCDF above background levels. Although present, and therefore a concern due to PCDD/PCDF's ability to bioaccumulate in humans, the fact that they are both known carcinogens and mutagens, as well as the potential impact from accumulation and biomagnification in aquatic and terrestrial food chains, the amount released during the DWH in-situ burns was concluded to be a minor portion of the overall annual U.S. inventory in 2009 (Gullett et al., 2016).

1.6.9 Carbonyls

According to Fingas et al. (1999), incomplete combustion of crude oil also produces low amounts of partially-oxidized materials, sometimes referred to as carbonyls or by their main constituents, aldehydes (formaldehyde, acetaldehyde, etc.) or ketones (acetone, etc.). Carbonyls from crude oil fires are, however, at very low concentrations and are well below health concern levels even close to the fire (Fingas, 2014b).

1.7 Distribution of Emissions

Fingas (2014b) concluded that the behavior of emissions is an important facet of oil spill burning because knowing how the various by-products of combustion are formed and behave can lead to a better understanding of burn site safe evacuation distances for response personnel and the general public. The overall emission behavior is illustrated in Figure 1. Previous studies have concluded that the most important compound to track and measure from a burn is particulate matter (Fingas, 2014b; Barnea, 1995; API, 2004; ADEC et al., 2008). The particulate matter initially rises and is then precipitated back to the ground, with the larger size (>10 μm) particulate matter settling at a rate of 0.3 m in less than 1 min. Before the plume travels 1 km, it is estimated that half of the particles larger than 10 μm have precipitated and fallen to the ground. Smaller particles may stay in the direction of the plume for a long time, and particles <0.5 μm take 5.5 hrs to settle 0.3 m. The average size particle produced by an in-situ burn is also 0.5 μm. As long as the plume rises and is not affected by any significant inversion, neither the visible plume nor the invisible combustion gasses should pose a threat to humans. However, some of the precipitated particulate matter could have other combustion by-products adsorbed, such as PAHs or PCDD/PCDFs. Water vapor and other light gasses such as CO, NO, VOCs and

carbonyls are distributed widely and soon reach background levels. CO_2 and other heavier-than-air gasses, such as SO_2 and NO_2, rise somewhat and then slowly sink to the ground.

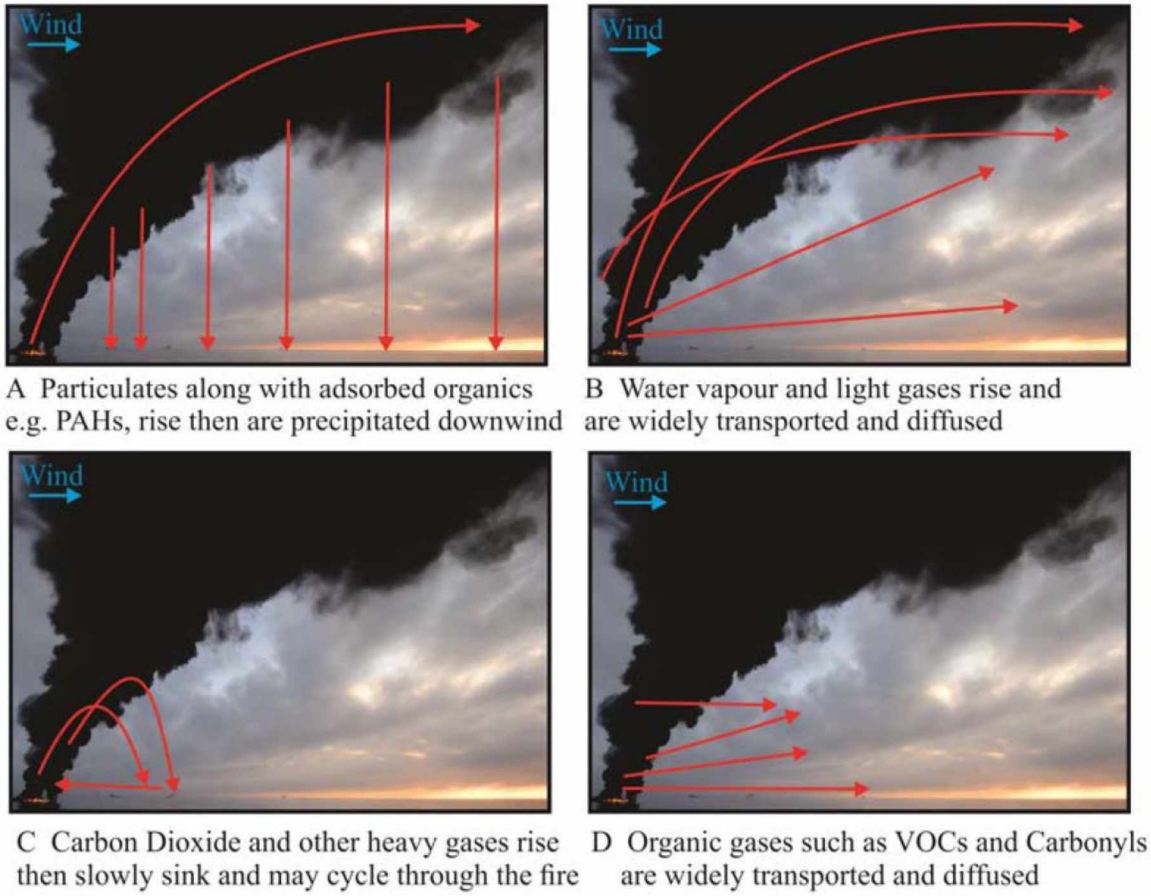

Figure 1 Behavior of particulate matter and the various combustion gasses produced during an in-situ burn (Fingas, 2014b).

1.8 Monitoring Requirements for In-Situ Burns

ADEC et al. (2008) stated in their guidance document "In-Situ Burning Guidelines for Alaska" that visual monitoring of the smoke plume is required for any crude oil and refined product burns in Alaska, and that air monitoring using instrumentation shall be conducted "where necessary" (pg. 59). When considered necessary, ADEC et al.'s (2008) guidelines require that monitoring is conducted according to the procedures outlined by the U.S. Coast Guard et

al.'s (2006) "Special Monitoring of Applied Response Technologies" (SMART) protocol. According to the SMART protocol, the established requirements are provided "for rapid collection of real-time, scientifically based information to assist the Unified Command with decision-making during in-situ burn operations" (pg. 31). The SMART protocol only requires the deployment of one monitoring team (three are recommended for large-scale burning operations) together with equipment to measure particulate matter (<10 μm) in real-time, a Global Positioning System (GPS) device, and some method to download and document or store the data collected. Taking into account wind direction and atmospheric conditions, the monitoring team is deployed to a location "where the potential exposure to the smoke may be most substantial (sensitive locations)" (pg. 32).

In Alaska, sensitive locations include populated areas, critical habitats for threatened and/or endangered species (e.g. sea lion rookeries), as well as archeological and historic resources (ADEC et al., 2008). Several "Class I Areas," which "receive a higher standard of air quality control to protect the visual quality of these scenic areas" (pg. 65), have also been established, and include Denali National Park & Preserve, Bering Sea Wilderness Area, Tuxedni Wilderness Area, and Simeonof Wilderness Area (ADEC et al., 2008). If there are several teams, one team shall be deployed to the upwind edge of the sensitive location while another team heads to the downwind edge. The same requirement applies to each sensitive location. The data collected shall be transferred to a Technical Specialist of the Incident Management Team, often located in the Planning Section of the command structure. The Technical Specialist then communicates the findings and his or her recommendations to the Unified Command.

1.9 Previous Studies Measuring Particulate Matter and Combustion Gas Concentrations

Several previous studies have been conducted where the concentration of particulate matter and the various combustion gasses have been measured during in-situ burns of crude oil. These studies ranged widely in the type and amount of crude oil burned, the size of the containment in which the burns were conducted, distance between the burn site and sampling location(s), where in relationship to the smoke plume the sampling station(s) was/were located, what type of sampling devices were used, and what combustion gases or sizes of particulate matter were measured. Much of the literature available on the emissions from an in-situ burn of crude oil has been written and rewritten as guidance documents when more information becomes available. Consequently, several of the studies in Table 1 use data from the same experiments or actual spill events. The methods utilized for this study most closely mimicked the experimental setup for the studies conducted by Mulholland et al. (1996), Devai et al. (1998) and Booher and Janke (1997).

Table 1 **Summary of literature review from previous studies conducted to measure emissions from ISBs.**

Reference	Oil Type; volume released; containment/basin size	Location of sampling stations	Results
Allen & Ferek (1993)	N/A (lit review)	N/A (lit review)	Stated that peak concentrations within the smoke plume about one-fourth to one-half mile downwind of an in-situ burn should be of the order of 100ppm for CO_2 , 1ppm for SO_2 and CO, 50ppb for NO_x, and about 1,000µg/m^3 for particulate matter.
Barnea (1995)	N/A (lit review)	N/A (lit review)	• Average SO_2 levels measured in experimental burns have been below 2ppm in the plume 100-200 meters downwind of the burn. • The concentration of NO_2 in the plume several miles downwind of the burn does not exceed several ppb. • The average level of CO in the smoke plume over the duration of the burns (15 to 30 minutes) was found to be 1-to-5ppm 150 meters downwind of the burns. While at several spots the concentration of particulates exceeded 150µg/m^3 even 16km downwind of the burn, other places in the plume had particulate concentrations lower than 150 µg/m^3. PM-10 concentration beneath the plume, 150-200 feet above the surface, did not exceed background levels of 30-to-40µg/m^3.
Booher & Janke (1997)	Turner Valley Crude Oil; 1893L; 6m x 6m basin	Plume & Ground station samplers (15-1500m from source); one test	• **Total Suspended Particulate (mg/m^3)** = 100, 125, 106 (plume); 8.1, 6.3, 0.36 (15m downwind); <0.2, <1.2, <0.18 (30m downwind). • **CO_2 (ppm)** = 1438 (plume); 466 (15m downwind); 354 (30m downwind). • **CO (ppm)** = 22 (plume). • **SO_2** = Not detected.
Devai et al. (1998)	South Lousiana Crude; 12.5L; 2.5m x 2.5m plot	Within the visible smoke plume; Shimadzu 14A gas chromatograph	Smoke plume concentrations of carbon dioxide averaged (four replications) 1,490ppm. No increases in NO and CO emissions were observed during burning.

Table 1, continued.

Fingas et al. (1993)	Not stated; 4830L & 2890L; 700ft fire boom	Three sampling stations: 50m, 100m, 500m downwind	**Burn 1:** **PM>10 (mg/m^3)** = 0.0 < 9.2 < 96.9; 0.0 < 14.0 < 15.7; 0.02 < 0.13 < 22.5 **Total VOCs (µg/m^3)** = 1143; 368; 721 **CO_2 (ppm)** = 50m downwind: average 900, max 970 **Burn 2:** **PM<10 (mg/m^3)** = 0.0 < 10.3 < 29.9; 0.0 < 12.3 < 35.0; 0.0 < 0.07 < 14.1 **CO_2 (ppm)** = 50m downwind average 850, max 950; 100m downwind average 900, max 920 **Summary:** • **Particulates:** It shows that particulates were at moderate levels under the plume at the locations sampled by the remote-controlled boats. Particulate levels dropped to background levels at the remote sampling station about 1 km downwind. • **PAHs:** comparison between the concentration of PAHs in the starting oil, residues, and soot shows that the PAHs are largely consumed by the fire. • **Aldehydes and ketones:** Data indicate that the concentrations are near background levels and actually are higher during the times when the oil is not burning. • **Dioxins and dibenzofurans:** The values are at background levels. This confirms previous studies that show that dioxins and dibenzofurans are not produced by fires. • **Total VOCs:** The levels of volatile organic compounds are well above concern levels, within 150 meters of the fire; however, the levels of these compounds are even greater from an evaporating slick that is not burning. • **Other combustion gasses:** Tests were made for a number of gasses, but CO and NO_x are not above the lower detection levels. Direct-reading instruments for SO_2 do not detect the compound above background levels. CO_2 plume moves close to the surface and that the gas has a distinct plume of its own, separate from the smoke plume.

Table 1, continued.

Fingas et al. (1996)	Not stated; 1300 to 14100L during 12 burns; burn area = 37.2-231m^2	Two sampling stations: 30m & 60m downwind, both on ground level (1.5m)	**Total particulates (µg/m^3)** = 112<752<8995; 30<299<3075 **SO_2 (ppm)** = LDL<0.68<1.20 at station 1 **CO_2 (ppm)** = 472<512<570; 387<426<500 **Total VOC (µg/m^3)** = 1224.03 average at station #1 • **PAHs:** additional PAHs are not produced by in situ oil fires. Oils contain significant quantities of PAHs. These are largely destroyed in combustion. The PAH concentrations in the smoke, both in the plume and the particulate precipitation at ground level are much less than the starting oil. These large soot particles adsorb appreciable quantities of multi-ringed PAHs. • **Particulate matter:** The concentration of particulates in the smoke plume may not be a significant concern past about 60 m. • **Dioxins and dibenzofurans:** Tests on the particulate matter both upwind and downwind of the fires show that these compounds are not produced during in situ crude oil fires. • **CO_2:** Concentration is well below concern levels, even near the fire. The distribution of the gas is very widespread, especially in low wind conditions. • **CO:** Very little produced by large-scale fires, concentrations are well below concern levels. • **SO_2:** Concentration is far below what is expected from the sulfur content of the oil. • **NO_x:** Tests were performed, however, no gasses above the background were detected. **VOCs:** Well above concern levels within 60 m of fires of this size.
Fingas et al. (1999)	N/A (lit review)	N/A (lit review)	• **CO_2:** Levels near a burn can be around 500 ppm. Concentrations of carbon dioxide are highest at the 1 m level and fall to background levels at the 4 m level. Concentrations at ground level are as high as 10 times that of the plume. • **CO:** Carbon monoxide levels are usually at or below the lowest detection levels of the instruments. The gas has only been measured when the bum appears to be inefficient, such as when water is sprayed into the fire. • **SO_2:** Sulphur dioxide is usually not detected at significant levels or sometimes not even at measurable levels. • **Other gasses:** Attempts were made to measure NO_x and other fixed gasses which might be the result of combustion. None were measured in about 10 experiments.

Table 1, continued.

Gullett et al. (2016)	MS252; unknown volume or containment size (ISB during DWH)	A 4.0m diameter, helium-filled aerostat was used to loft an instrument package into the in situ oil fire plumes	Provided the only known analysis of samples from an actual spill. PCDD/PCDF levels confirmed detection from the combustion process, disputing others' previous claims. The observed PAHs were consistent with previous at-sea burn simulations albeit at lower concentrations.
Middlebrook et al. (2011)	MS252; unknown volume or containment size (ISB during DWH)	200m elevation; aircraft flew a rectangular pattern about 8 km from the DWH site and then flew transects perpendicular to the wind direction at progressively farther distances downwind.	• **Total Particulate matter:** Maximum 18.8µg/m^3 around spill/burn site, 25.9µg/m^3 downwind (unknown distance) on June 8; Maximum 8.1 µg/m^3 around spill/burn site, 15.5 µg/m^3 downwind (unknown distance) on June 10. • **NO_x:** Maximum 0.3ppbv at the drill site, 0.25ppbv 13km downwind. • **CO:** Maximum 152ppbv around spill/burn site, 163ppvb downwind (unknown distance) on June 8; Maximum 143ppbv around spill/burn site, 152ppvb downwind (unknown distance) on June 10. • **NO_2:** Maximum 0.5ppbv around spill/burn site, 1.3ppvb downwind (unknown distance) on June 8; Maximum 4.4ppbv around spill/burn site, 1.5ppvb downwind (unknown distance) on June 10.
Mulholland et al. (1996)	80% murbana & 20% Arabian crude oil; volume = 2cm of oil on top of water; containment size either 1m diameter or 2.7m x 2.7m	In-plume measurements from a height of 4.0m using a CO-CO_2 nondispersive infrared analyzer.	The nominal average values were 2000 ppm for CO_2, and 40ppm for CO, for both the 1m and the 2.7-m pans.

1.10 Previous Studies Evaluating the Fate and Transport of Herding Agents

The fate of the herding agent during and after an in-situ burn previously has not been studied in detail. The reason for this is unknown, but may be due to the low amount recommended to be applied and the low toxicity of the two currently approved herding agents. If

after an in-situ burn the herding agent remains on the water surface and does not sink, mixes with the oil residue, or is emitted through the smoke plume, initial biodegradation tests conducted by Ross, et al. (2015) indicate that ThickSlick 6535 will biodegrade rapidly (100% degraded at day 22), and OP-40 will biodegrade more slowly (19% degraded at day 28). It should be noted that these studies were conducted at normal room temperature, and not in the colder temperatures of the arctic. Toxicity testing is required to list a product on U.S. EPA's National Contingency Plan Product Schedule. Ross et al. (2015) found that ThickSlick 6535 was "practically non-toxic" (as defined by the U.S. EPA's aquatic toxicity ranking system), while the OP-40 had somewhat greater toxicity (Ross, 2015). In comparison, both the ThickSlick 6535 and the OP-40 had a lower toxicity than a #2 Fuel Oil. However, a 1:10 mix of either the ThickSlick 6535 or OP-40 and the #2 Fuel Oil was found to be more toxic than the No. 2 fuel oil by itself. In that regard, it should be noted that neither of the herding agents is supposed to be mixed with the petroleum product intended for burning, they should be applied in a perimeter around the slick, and that the application rate utilized during the toxicity tests was 30 times higher than the manufacturer designed application rate (Ross et al., 2015).

2 Materials and Methods

2.1 Site Description

Five ISB field tests were conducted in April 2015 at Poker Flat Research Range (PFRR), a test facility owned by the University of Alaska Fairbanks and located approximately 50 kilometers north-northeast of Fairbanks, Alaska (Figure 2a).

Figure 2 **(a) Location of PFRR in Alaska (Microsoft Bing Maps®, 2016); and (b) aerial view of the test basin and test site (Potter et al. 2016).**

The test site consisted of a 90-by-90 m lined and bermed containment area, which was filled with 15-to-20 cm of fresh water during the dates of the experiment and had approximately 6% ice and faux iceberg coverage (Figure 2b).

2.2 ISB Field Tests

Five tests were conducted (April 22 –April 27, 2015) and during each test, 70-to-155 L of Alaska North Slope (ANS) crude oil was released from a 2.4-by-2.4 m metal containment located within the basin (Figure 3a). The crude oil was transported to the release point in 18.9 L capacity containers and then transferred to the containment area by pouring the product into the release frame (Figure 3a). The herding agent, 1-to-11 L of Siltech OP-40 or ThickSlick 6535, was ground-applied via hand-held 3.78 L capacity garden sprayer or aerially applied via a helicopter mounted application system manufactured by Desmi, Inc (Figure 3b). Ignition was accomplished using standard Ziploc® bags containing gelled gasoline/diesel mixture, mounted on either a remotely controlled vessel, transferred to the slick by hand, or by utilizing a helicopter mounted helitorch containing the same mixture (Figure 3c). The flammable mixture is ignited when exiting the helitorch and applied from above on to the herded oil slick. Ignited oil slick was then herded to various locations around the basin depending on wind direction, wind speed, and success of herding agent application. Table 2 contains a summary of test parameters, including burn efficiency.

Figure 3 **Please see caption on next page.**

Figure 3 **(a) Alaska Clean Seas (ACS) responders carry crude oil and release containment; (b) Helicopter herding agent application system (Buist et al., 2014); (c) Ignition process using helitorch.**

Table 2 **Summary of test parameters and results (Aggarwal et al., 2017).**

Test and Date (Year 2015)	Volume of Oil Added (ANS Crude)	Herding Agent (Volume, Type)	Heli Torch Fuel Mix (diesel : gasoline)	Wind Speed (m/s)	Air Temperature (°C)	Burn Efficiency (Gravimetric)	Max. Slick Area Prior to Contact with Wall (m^2)
Test 1, April 22	70 L	11 L, OP-40	60 % : 40 %	1.0 -1.5	6 – 7	86 %	101
Test 2, April 23	75 L	4 L, OP-40	0 % : 100 %	3.3 – 5.7	10	59 %	193
Test 3, April 24	151 L	5 L, OP-40	20 % : 80 %	2.9 – 5.0	13	94 %	185
Test 4, April 25	155 L	1 L, TS 6535	20 % : 80 %	1.0 – 2.0	12	73 %	277
Test 5, April 27	155 L	4 L, TS6535	20 % : 80 %	3.4 – 6.1	15	86 %	157

2.3 Atmospheric Sampling and Data Collection

To conduct real-time monitoring of downwind, in the smoke plume, concentrations of combustion gasses and particulate matter, instruments displayed in Table 3 were used and located as shown in Figures 4 and 5. The reader should note that none of the instruments or methods utilized during the tests to measure atmospheric conditions are standard methods established and approved by either OSHA or NIOSH. Data collection was initiated at least five minutes before ignition occurred and continued at least until five minutes after combustion had ceased. The VOC and $NO/NO_2/NO_x$ instruments did not have data logging capabilities, so data was recorded by utilizing a video camera to record the real-time concentrations projected on the instrument display. After every test, the data were downloaded from every instrument, utilizing software provided by the manufacturer. For data recorded using a video camera, footage was analyzed and data recorded in one to five-second intervals, depending on the instrument.

Table 3 Instruments utilized for logging particulate matter and combustion gas concentrations.

Compound(s) measured	Manufacturer	Model	Utilized during test no?	Instrument range (resolution)
CO & CO2	TSI	Q-TRAK IAQ Monitor, Model 8550/8551	2, 3, & 5	CO2: 0-5000ppm (1 ppm) CO: 0-500ppm (1 ppm)
PM-1, PM-2.5, or PM-10	TSI	DUSTTRAK Aerosol Monitor, Model 8520	2, 3, & 5	1-100 mg/m3 (1 ppm)
SO2	RAE Systems	ToxiRae Pro with SO2 Sensor	2, 3, & 5	0-20 ppm (0.1 ppm)
NO, NO2, & NOx	IMR Environmental Equipment, Inc.	IMR 2800 P	2	NO: 0-2000ppm (1 ppm) NO2: 0-100ppm (1 ppm) NOx: 0-NOx max (1 ppm)
NO, NO2, & NOx	ThermoFisher	NOx Analyzer Model 42C	3 & 5	1-999 ppb (0.1 ppb)
VOCs, 0-15,000ppm	RAE Systems	PPM VOC Monitor: MiniRAE 3000	2, 3, & 5	1-15,000 ppm (0.1 ppm)

All the CO/CO_2, SO_2, $NO/NO_2/NO_x$, and VOC measuring instruments were calibrated before Test 1 on April 22, 2015, by the factory or by using applicable calibration gasses according to procedures provided by the manufacturer for each instrument. All instruments were within 1% of expected results during the calibration effort. Calibration data was recorded.

Figure 4 Flatbed trailer and ATV utilized to reposition the sampling station.

The instruments were placed 1.5m above ground, which is the standard receptor height for humans and a height utilized by previous studies (Fingas, 2014a). Instruments were staged on a 2.5-by-2.5 m flat-bed trailer towed by an All-Terrain Vehicle (ATV). The instrument setup enabled repositioning of the sampling station after ignition had occurred to increase the chance of collecting data downwind, in the smoke plume (Figure 3). For three out of five test burns, the instruments were located 6-to-12 m downwind of the combustion location in the basin (during Test 2, Test 3, and Test 5 on April 23, 24, & 27, 2015, respectively), and wind speed was adequate to collect readings downwind in the smoke plume (Figure 4 & 5). Wind direction and

speed were not favorable for the collection of readings or samples downwind in the smoke plume during Test 1 and Test 4 on April 22 & 25, 2015, respectively. Data from those tests is therefore not included in this analysis.

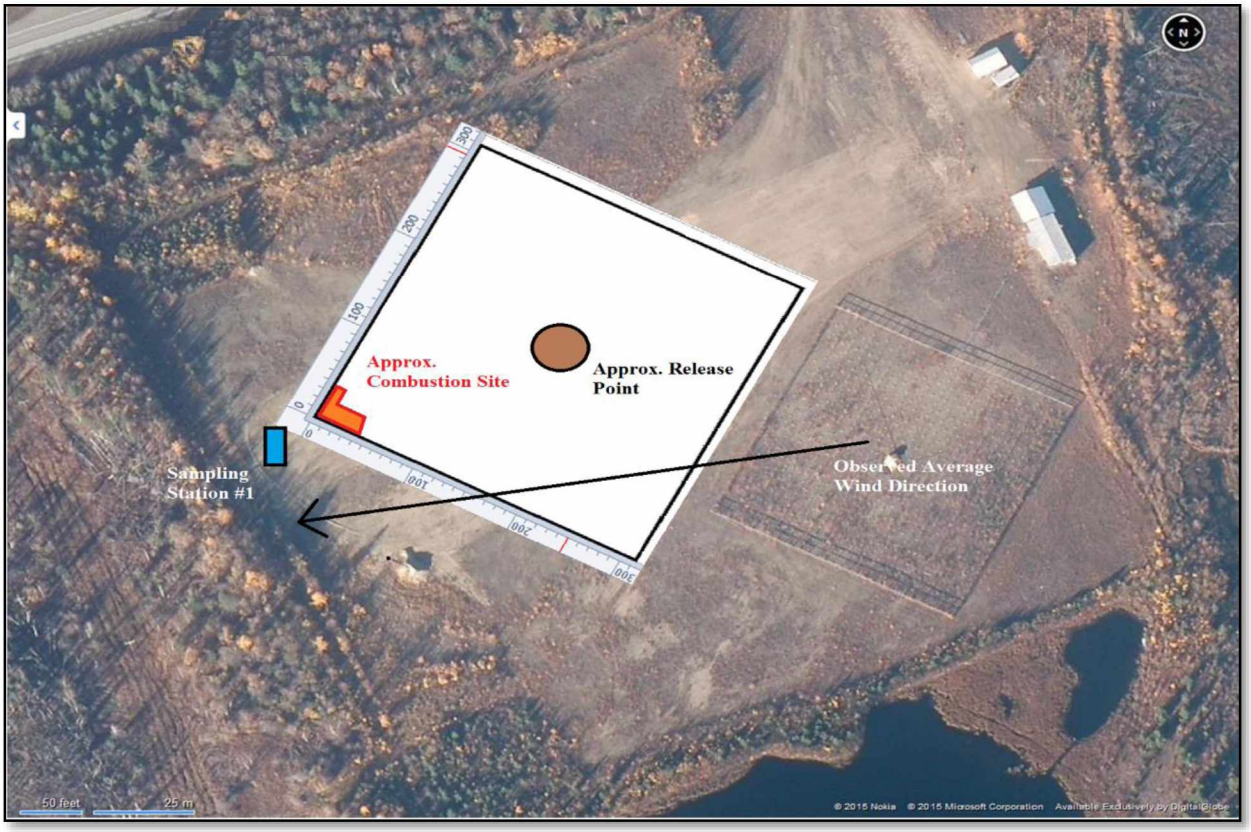

Figure 5 **Site schematic for Test 2, Test 3, and Test 5, showing general wind direction during burn as well as location of sampling station, approximate combustion site in test basin, and approximate crude oil release point within test basin.**

Figure 6 **Sampling event on April 23, 2015 (Test 2), showing sampling station (tripod of sampling equipment visible along right edge) in relation to airborne plume during ISB.**

2.4 Herder Analysis

To determine if applied herder was volatilized and present in the emission plume, an air sampling pump (SKC AirChek 2000) was deployed in conjunction with tubes containing granular activated carbon (GAC) and was placed downwind, in the smoke plume. The reader should note that the collected air samples were only analyzed for the herding agent functional group, and no other compounds such as particulate matter, VOCs, or PAHs. The pump has an internal flow sensor to measure flow rate with an accuracy of ±5%, and the flow rate was set at 1500 mL/min during the tests. The flow was initiated at least five minutes before ignition and continued until at least five minutes after combustion had ceased. The sample tubes were transported to the laboratory within three hours and stored at 4°C. To investigate the presence of herder, gas chromatography-mass spectroscopy (GC/MS) method was used. To prepare the

sample for GC/MS analysis, GAC was removed from the sorbent tube and placed in a 2mL autosampler vial. One milliliter of carbon disulfide and 100 µL of D-5 nitro-benzene (internal standard) were added to the vial. The vial was immediately capped and then mixed by inverting the vial at least five times before leaving undisturbed for 15 minutes. The GC/MS utilized was an Agilent 6890N CG and 5973N MS, with a Restek RTX-1 (catalog #10139), 100 % dimethylpolysiloxane, 30 m length, 0.32 mm inner diameter, and 0.5 µm film thickness column. Two microliters of each sample were then injected into the GC with an inlet temperature set at 300°C. Scan acquisition mode for the MS was set at 50-450 m/z.

To the author's knowledge, there are no standard methods established to quantify the utilized herding agent (Siltech OP-40) using GC/MS. An analysis method was established based on the chemical structure (Figure 6) found when searching for the CAS number (67674-67-3; ShangHai Original Economy – Trade Develop Co., Ltd., 2016) provided through the manufacturer's MSDS for OP-40 (Siltech, 2012). The herding agent appears to be a mix, with multiple values for "n" in the chemical formula. The octamethyl trisiloxane functional group appears to be a primary contributor to the mass spectrum because it is common in all peaks, and appears to be cleaved off when ionized. When analyzing pure herder for instrument calibration purposes, the results showed consistent retention times for the peaks and a linear response with concentration.

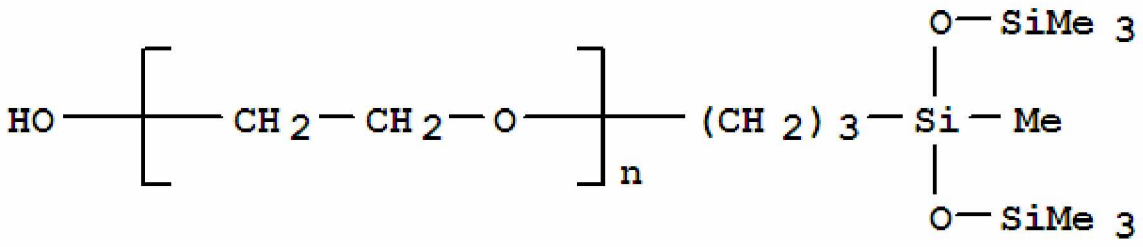

Figure 7 **Chemical structure for Siltech OP-40 (ShangHai Original Economy – Trade Develop Co., Ltd., 2016).**

2.5 Data Analysis

To answer the question related to real-time monitoring of combustion gases and particulate matter downwind, in the smoke plume, concentrations, downloaded data was analyzed in Microsoft Excel 2013® using a one-sample t-Test, either one or two tailed, to determine if maximum or average concentration, for each compound of interest, collected during each experiment was significantly below or above the established:

- OSHA Time Weighted Average (TWA) Permissible Exposure Limit (PEL) and Short-Term Exposure Limit (STEL).
- NIOSH Time Weighted Average (TWA) Recommended Exposure Limit (REL), NIOSH Short Term Exposure Limit (ST), and the NIOSH Immediately Dangerous to Life & Health (IDLH).
- EPA's National Ambient Air Quality Standard (NAAQS) 1, 8, and 24 hr averaging times.

A summary of the various limits can be found in Table 4 below.

Table 4 NAAQS, STEL, ST, IDLH, and TWA RELs and PELs established by EPA, OSHA, & NIOSH (CDC, 2015; USDOL, 2013; & EPA, 2017).

Compound	OSHA PEL (STEL or C)	NIOSH REL (ST)	NIOSH IDLH	OSHA PEL (TWA)	NIOSH REL (TWA)	NAAQS 1hr	NAAQS 8hrs	NAAQS 24hrs
CO (ppm)	**200**	**200**	**1,200**	**50**	**35**	**35**	**9**	*N/A*
CO_2 (ppm)	**30,000**	**30,000**	**40,000**	**5,000**	**5,000**	*N/A*	*N/A*	*N/A*
SO_2 (ppm)	**5**	**5**	**100**	**5**	**2**	**0.075**	*N/A*	*N/A*
PM-2.5 (mg/m^3)	*N/A*	*N/A*	*N/A*	**5**	*N/A*	*N/A*	*N/A*	**0.035**
NO (ppb)	*N/A*	*N/A*	**100,000**	**25,000**	**25,000**	*N/A*	*N/A*	*N/A*
NO_2 (ppb)	**5,000**	**1,000**	**20,000**	*N/A*	*N/A*	**100**	*N/A*	*N/A*
NO_x (ppb)	*N/A*	*N/A*	*N/A*	*N/A*	*N/A*	*N/A*	*N/A*	*N/A*
VOCs (ppm)	*N/A*	*N/A*	*N/A*	*N/A*	*N/A*	*N/A*	*N/A*	*N/A*

The one-sample t-Test was conducted by determining the average maximum concentrations, as well as the null value (PEL, REL, or NAAQS) and standard error, for each combustion gas and particulate matter size collected during the second, third, and fifth test, then finding the t-value using Equation 1. The obtained t-value was then utilized to calculate the Student's T distribution in Microsoft Excel 2013®, using the "TDIST" function, which is a continuous probability distribution that is frequently used for testing hypotheses on small sample data sets. For this study, either a one or two-tailed distribution with a significance threshold of $P< 0.01$ or $P<0.005$, respectively, was used because the question posed was to determine if the average concentration of each combustion gas and particulate matter size was significantly above or below the applicable exposure limits or air quality standards.

$$t = \frac{sample\ mean - null\ value}{standard\ error} \qquad \text{(Eq. 1)}$$

To determine the presence or absence of emitted herding agent functional groups, chromatograms created by the instrument during analysis of pure Siltech OP-40 were initially reviewed to identify potential absorbance peaks created by the herding agent. The initial review showed ions with a mass-to-charge ratio of 191, 207, and 221, which were then used for quantitative calculation when analyzing the air samples.

2.6 Wind Analysis

In order to determine any potential correlation between wind speed and a number of combustion gasses produced, this study utilized two different devices to log wind speed as well as direction. A Met One E-BAM Real-Time Beta Gauge with an EX-034 Wind Speed and

Direction Sensor (Figure 8c) had been placed on a level surface along (within 20 ft) the northwest edge of the burn basin (Figure 8a) and calibrated to true north. Another device capable of measure wind speed and direction, a Campbell Scientific CR1000 Measurement and Control Datalogger with an RM Young 05103 Wind Monitor, had been set up on a level surface approximately 200 ft to the east of the basin and calibrated to true north.

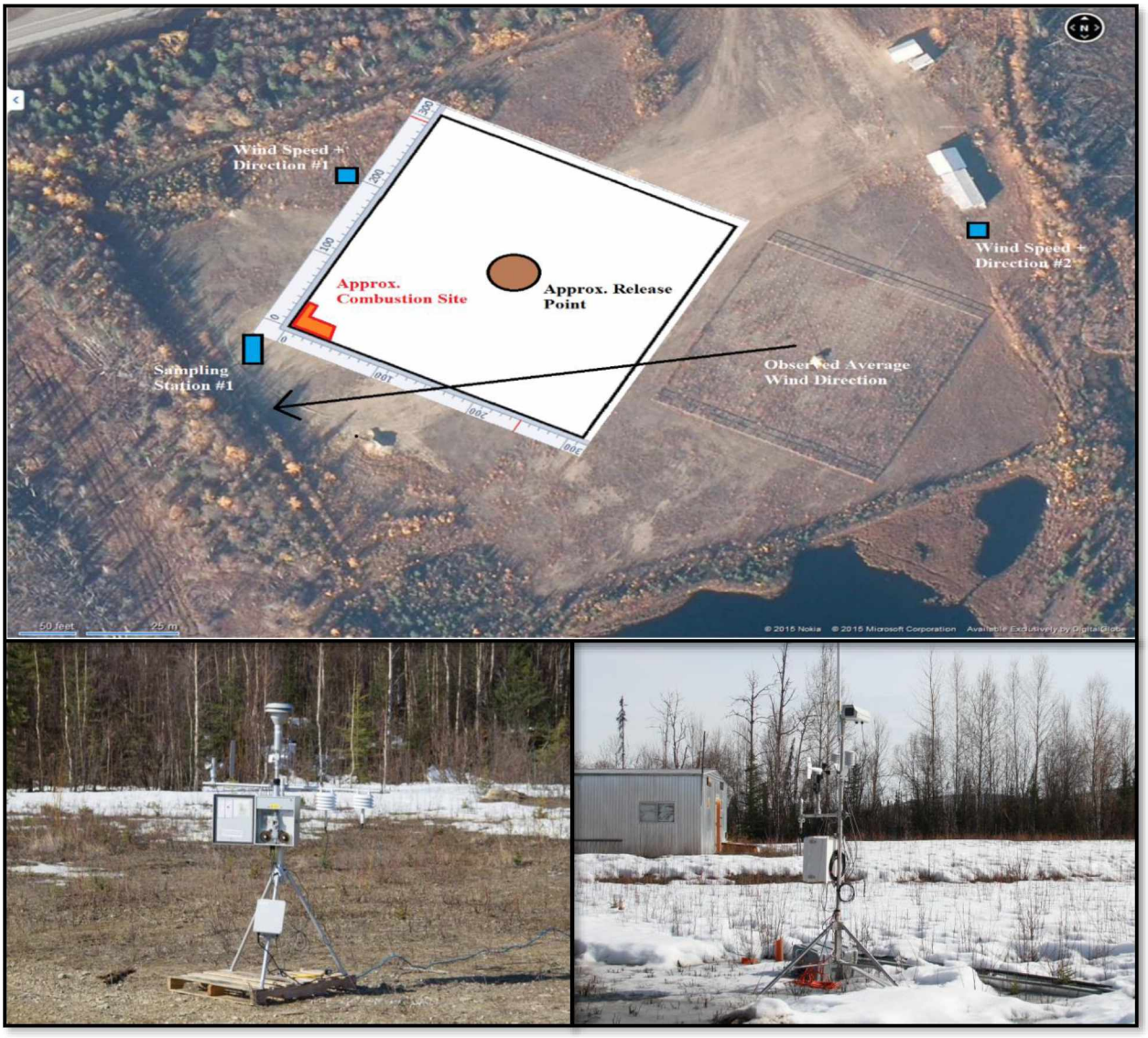

Figure 8 **(a) Schematic of PFRR burn site, with wind speed + direction station #1 & #2 depicted; (b) Met One E-BAM at wind speed + direction station #1 (Potter et al., 2016); (c) Campbell Scientific CR1000 Datalogger at wind speed + direction station #2 (Potter et al., 2016).**

3 Results and Discussion

Wind direction was favorable during Tests 2, 3, and 5 (for conducting measurements downwind, in the smoke plume) due to the fact that the released and ignited crude oil was mobilized by both the herding agent and the wind towards the northwest corner of the test basin. Due to the metal flashing located at the bottom the dike wall along each side of the basin, the crude and herder mixture combusted only 6-to-12 m upwind of the air sampling instruments. The wind speed was then adequate to carry the airborne plume towards the instruments, allowing for measurements of the various combustion gas and particulate matter concentrations in the downwind smoke plume as well as the collection of air samples to be analyzed for the presence or absence of the herding agent.

3.1 Results and Discussion Related to Atmospheric Sampling and Data Collection

Figure 9 below contains CO_2 data, shown with 15 sec intervals, collected during Tests 2, 3, and 5. The maximum measured CO_2 concentrations during Test 2, Test 3, and Test 5 were 2930 ppm, 1584 ppm, & 1229 ppm, respectively. The average maximum concentration measured for the three tests was 1784 ± 710 ppm. The average concentration measured during the three burns was 530 ± 67 ppm. To make the graph less crowded, the average concentration from the two instruments utilized during each of the burns is depicted. Figure 10 contains CO_2 concentrations measured during Tests 2, 3, and 5, with data presented as boxplots, and compared to applicable exposure limits. The blue square of each plot represents the average concentration for each test. It should be noted that two instruments, with the same specifications, were utilized during each burn, and that concentrations on the Y-axis are on a base-10 logarithmic scale.

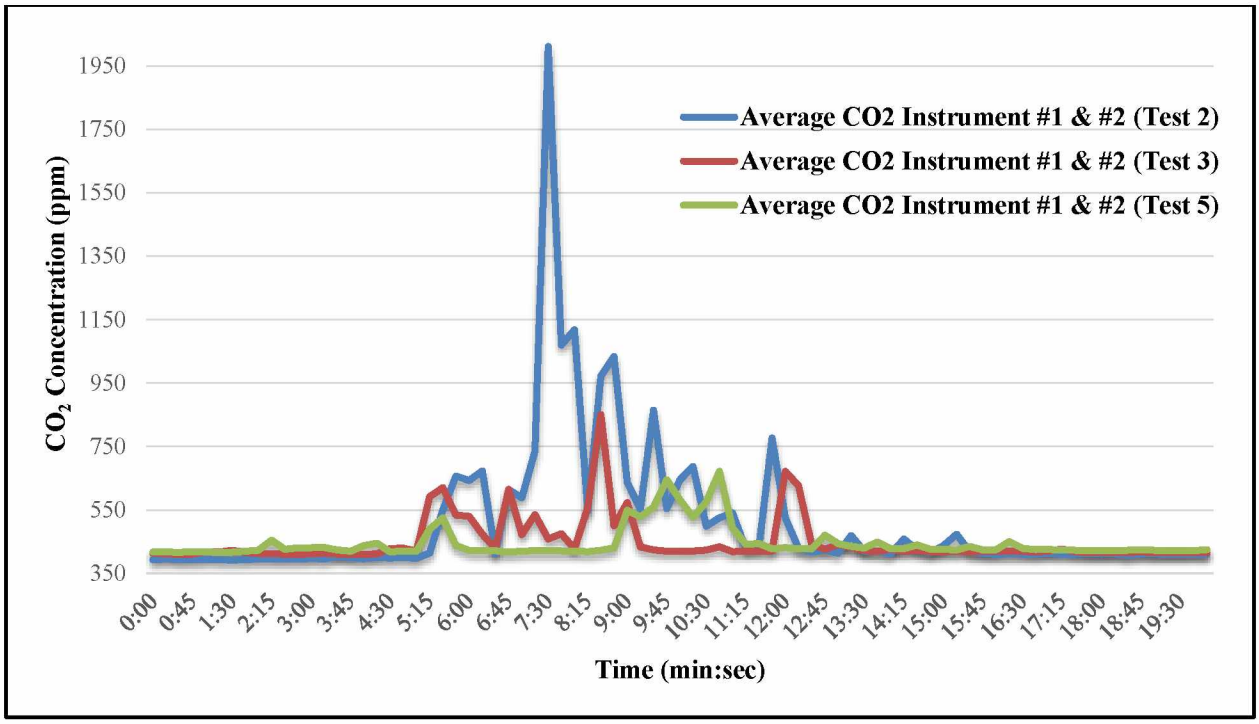

Figure 9 **CO_2 concentrations measured during Test 2, 3, & 5, depicted at a 15sec interval.**

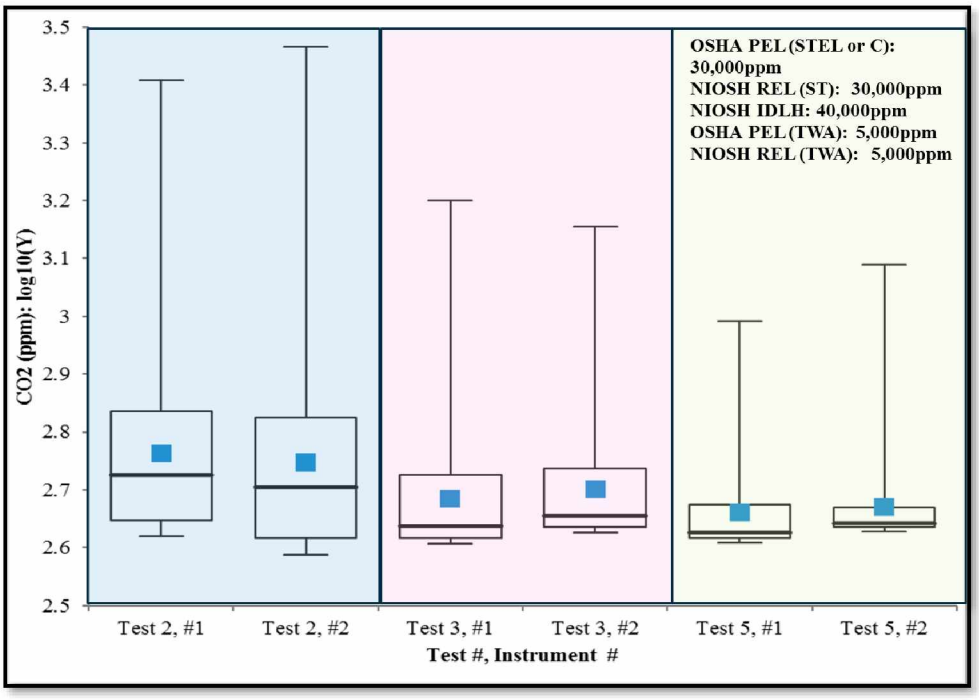

Figure 10 **Box plots are showing measured CO_2 concentrations during burns, in comparison to established exposure limits and air quality standards. Average concentrations marked with a blue square. Concentrations on the Y-axis is on a base-10 logarithmic scale.**

Figure 11 below contains CO data, shown with 15sec intervals, collected during Tests 2, 3, and 5. The maximum measured CO concentrations during Test 2, Test 3, and Test 5 were 33 ppm, 23 ppm, & 9 ppm, respectively. The average maximum concentration measured for the three tests was 20 ± 8 ppm. The average concentration measured during the three burns was 4 ± 1 ppm. To make the graph less crowded, the average concentration from the two instruments utilized during each of the burns is depicted. Figure 12 contains CO concentrations measured during Tests 2, 3, and 5, with data presented as boxplots, and compared to applicable exposure limits and air quality standards. The blue square of the plots represents the average concentration for each test. It should be noted that two instruments, with the same specifications, were utilized during each burn, and that concentrations on the Y-axis are on a base-10 logarithmic scale with a constant (y+1) added to each data point.

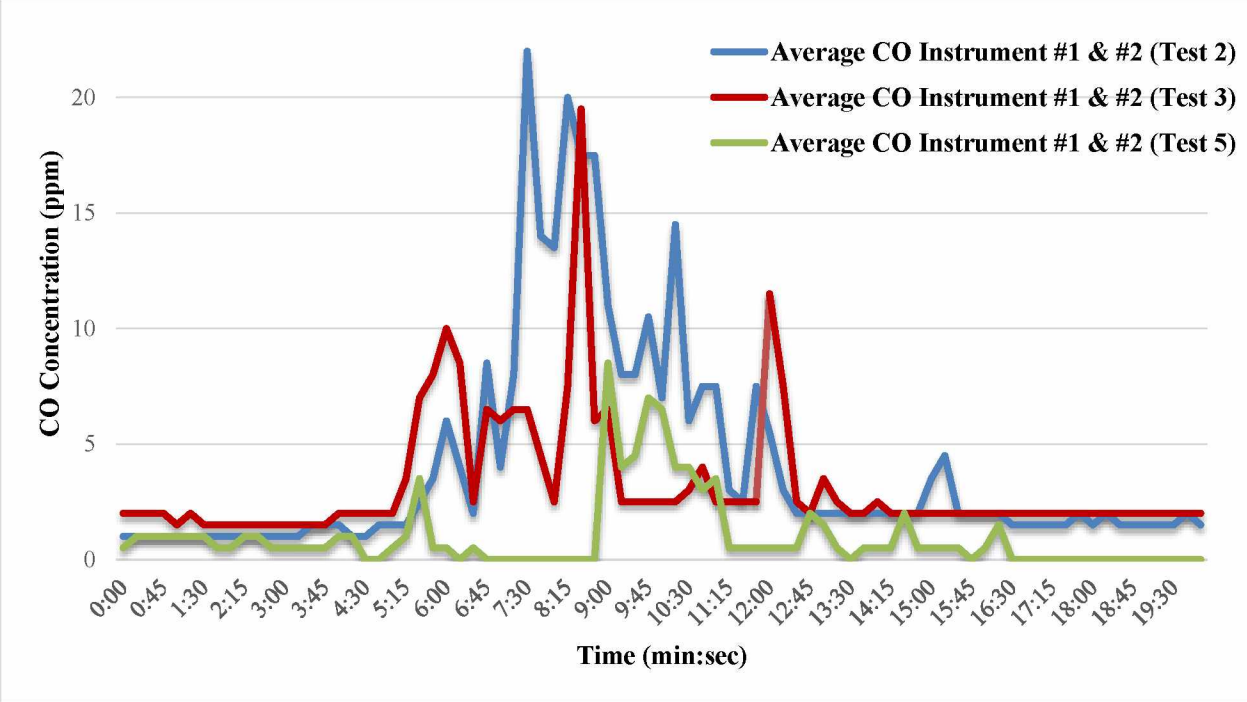

Figure 11 **CO concentrations measured during Test 2, 3, & 5, depicted at a 15sec interval.**

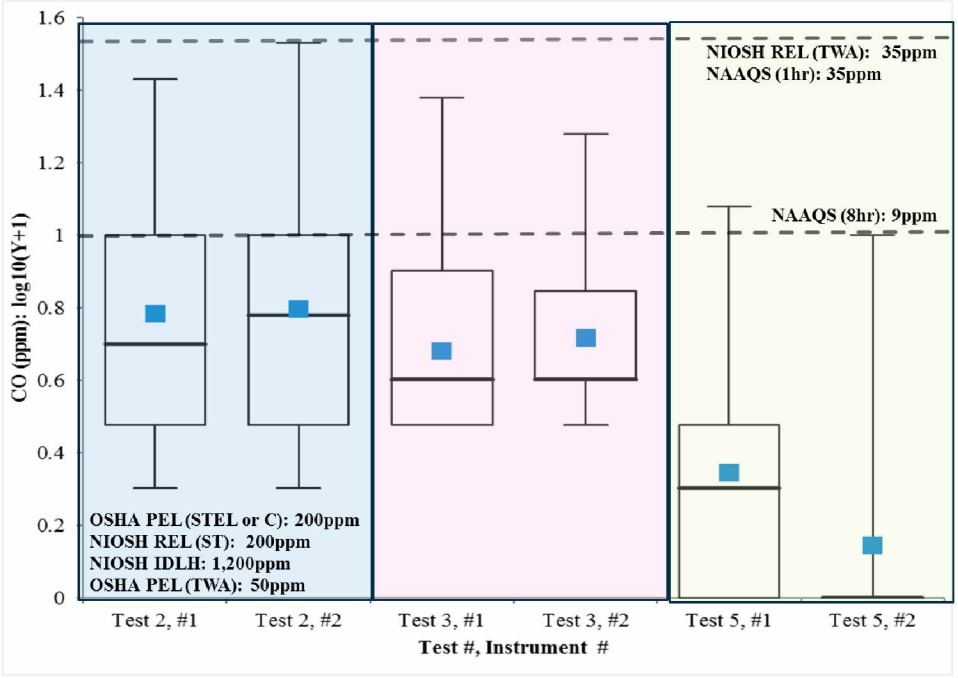

Figure 12 **Box plots are showing measured CO concentrations during burns, in comparison to established exposure limits and air quality standards. Average concentrations marked with a blue square. Concentrations on the Y-axis is on a base-10 logarithmic scale, with a constant (y+1) added to each data point.**

Figure 13 below contains PM-2.5 data, shown with 15 sec intervals, collected during Tests 3 and 5 (no PM-2.5 data was collected during Test 2). The maximum measured PM-2.5 concentrations during Test 3 and Test 5 were 202.27 mg/m^3 and 206.34 mg/m^3, respectively. The average maximum concentration measured for the three tests was 204.26 ± 2.04 mg/m^3. The average concentration measured during the three burns was 9.60 ± 3.50 mg/m^3. Figure 14 contains PM-2.5 concentrations measured during Tests 2, 3, and 5, with data presented as boxplots, and compared to applicable exposure limits and air quality standards. The blue square of the plots represents the average concentration for each test. It should be noted that concentrations on the Y-axis are on a base-10 logarithmic scale with a constant (y+1) added to each data point.

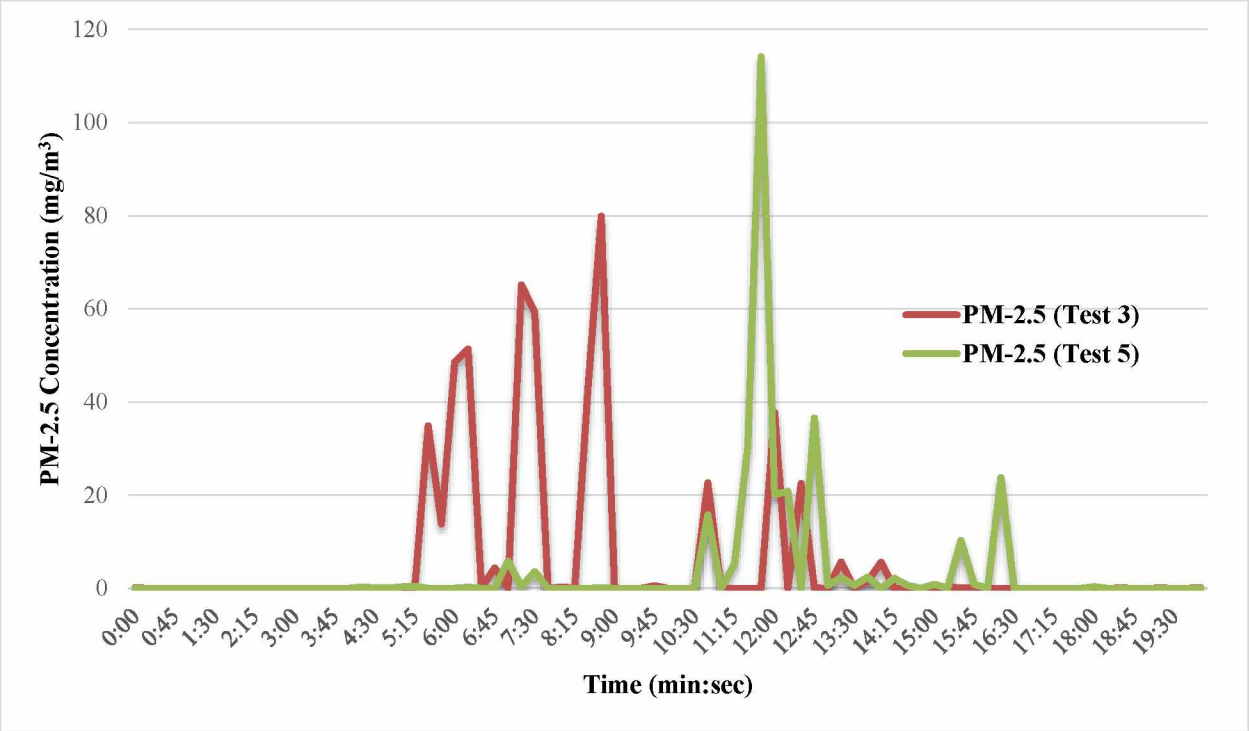

Figure 13 **PM-2.5 concentrations measured during Test 3 & 5, depicted at a 15sec interval.**

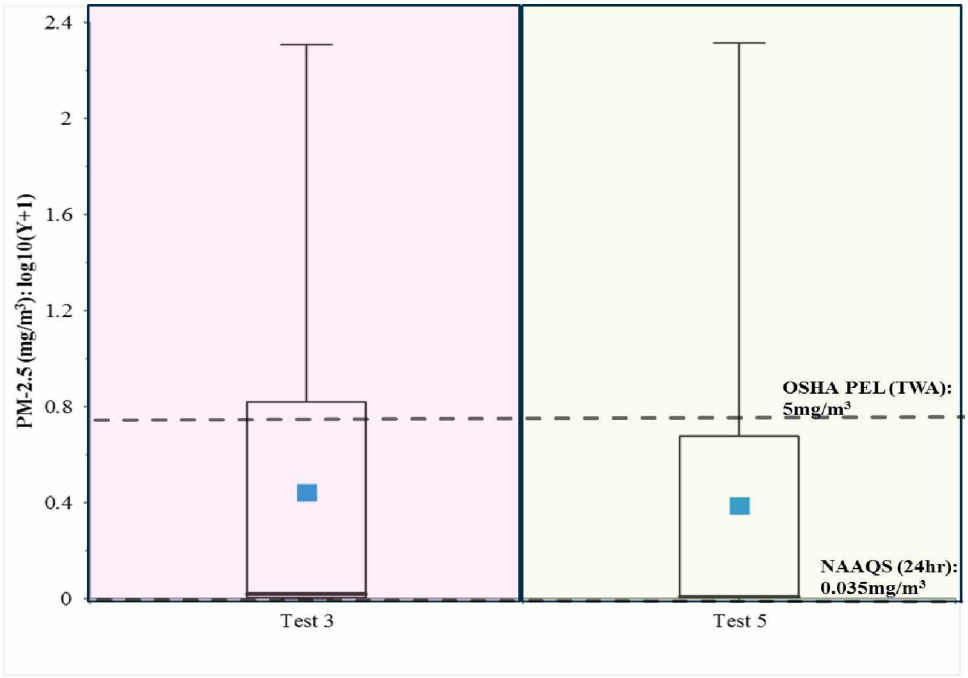

Figure 14 **Box plots are showing measured PM-2.5 concentrations during burns, in comparison to established exposure limits and air quality standards. Average concentrations marked with a blue square. Concentrations on the Y-axis is on a base-10 logarithmic scale, with a constant (y+1) added to each data point.**

Figure 15 below contains SO_2 data, shown with 15 sec intervals, collected during Tests 2, 3, and 5. The maximum measured SO_2 concentrations during Test 2, Test 3, and Test 5 were 4.8 ppm, 3.7 ppm, and 2 ppm, respectively. The average maximum concentration measured for the three tests was 3.4 ± 1.1 ppm. The average concentration measured during the three burns was 0.5 ± 0.2 ppm. To make the graph less crowded, the average concentration from the two instruments utilized during each of the burns is depicted. Figure 16 contains SO_2 concentrations measured during Tests 2, 3, and 5, with data presented as boxplots, and compared to applicable exposure limits and air quality standards. The blue square of the plots represents the average concentration for each test. It should be noted that two instruments, with the same specifications, were utilized during each burn, and that concentrations on the Y-axis are on a base-10 logarithmic scale with a constant (y+1) added to each data point.

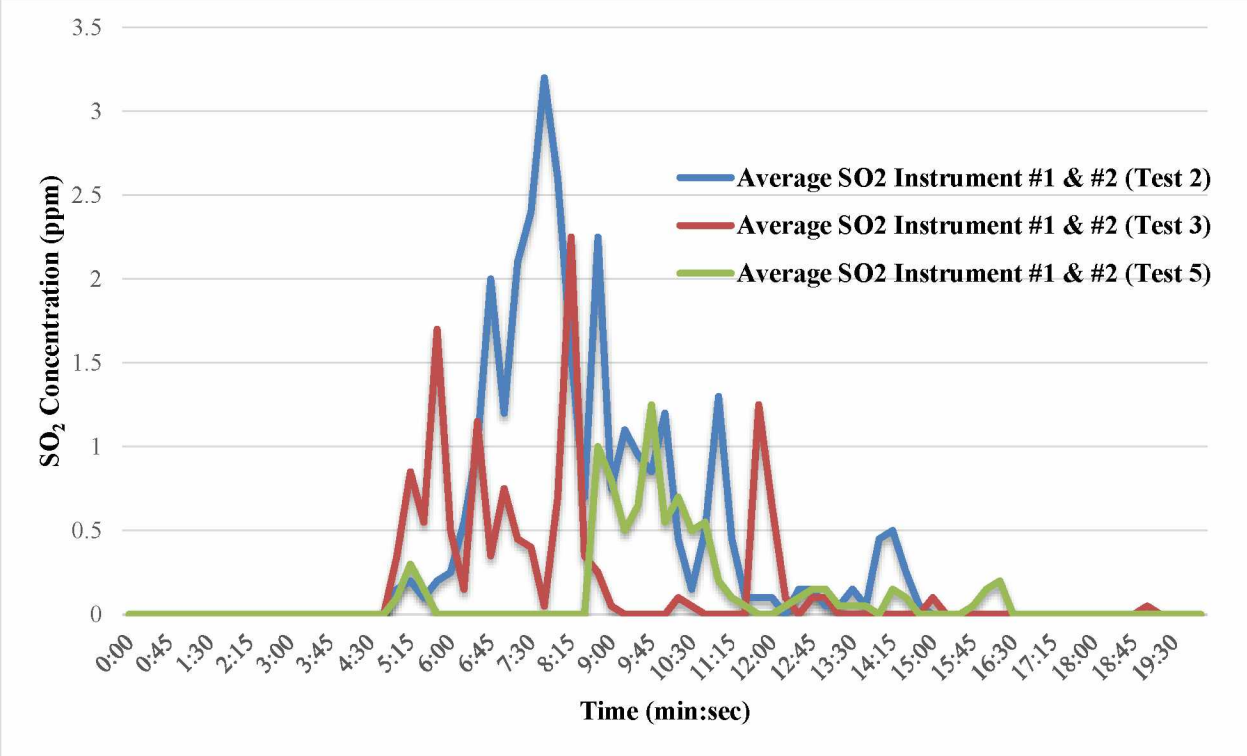

Figure 15 **SO_2 concentrations measured during Test 2, 3, & 5, depicted at a 15sec interval.**

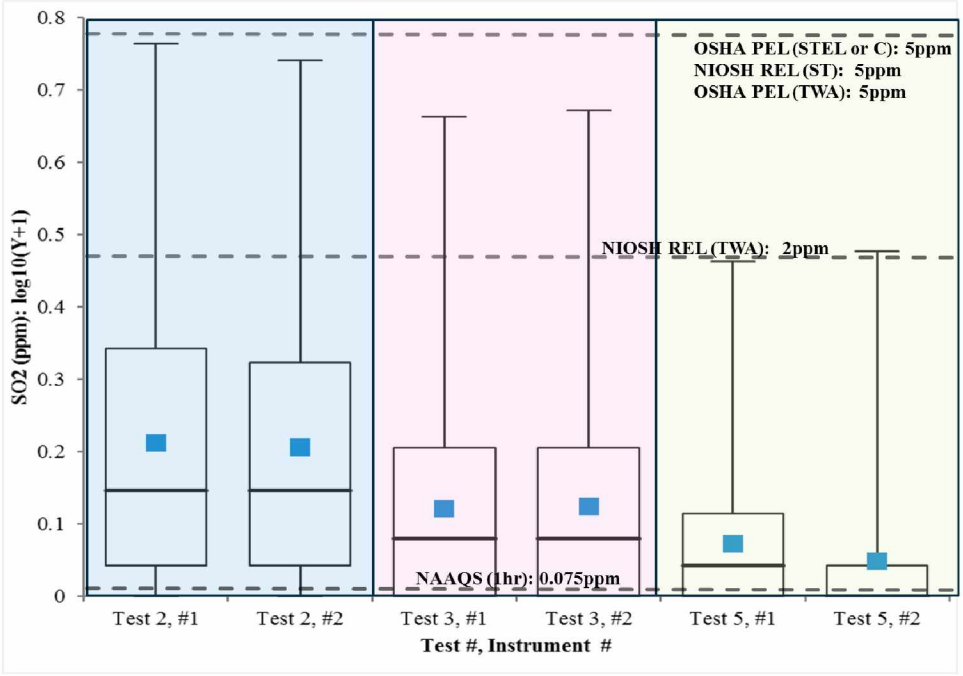

Figure 16 **Box plots are showing measured SO_2 concentrations during burns, in comparison to established exposure limits and air quality standards. Average concentrations marked with a blue square. Concentrations on the Y-axis is on a base-10 logarithmic scale, with a constant (y+1) added to each data point.**

Figure 17 below contains NO data, shown with 15 sec intervals, collected during Tests 2, 3, and 5. Two different instruments were used for sample collection, with the one utilized for Test 2 only being capable of logging concentrations in the ppm range. The maximum measured NO concentrations during Test 3, and Test 5 were 73 ppb and 46 ppb, respectively. The average maximum concentration measured for the three tests was 59.5 ± 13.5 ppb. The average concentration measured during the three burns was 21.1 ± 5.4 ppb. Figure 18 contains NO concentrations measured during Tests 2, 3, and 5, with data presented as boxplots, and compared to applicable exposure limits. The blue square of the plots represents the average concentration for each test.

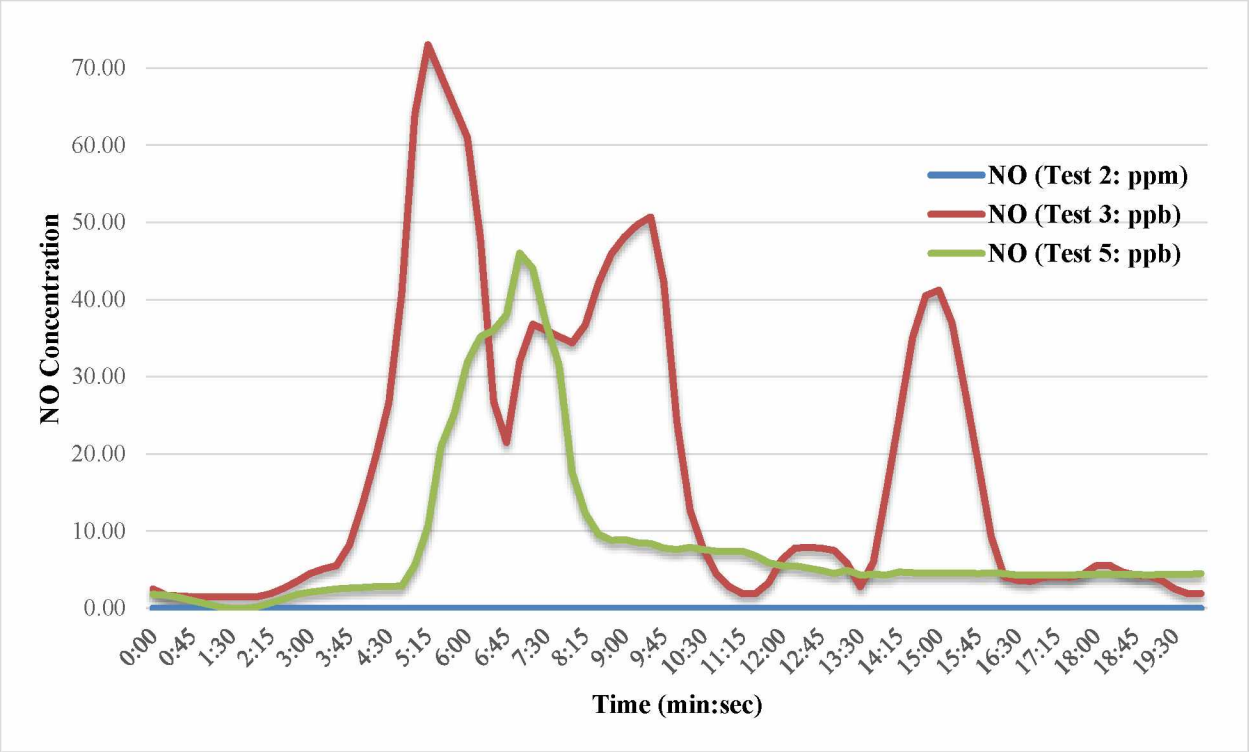

Figure 17 **NO concentrations measured during Test 2, 3, & 5, depicted at a 15sec interval.**

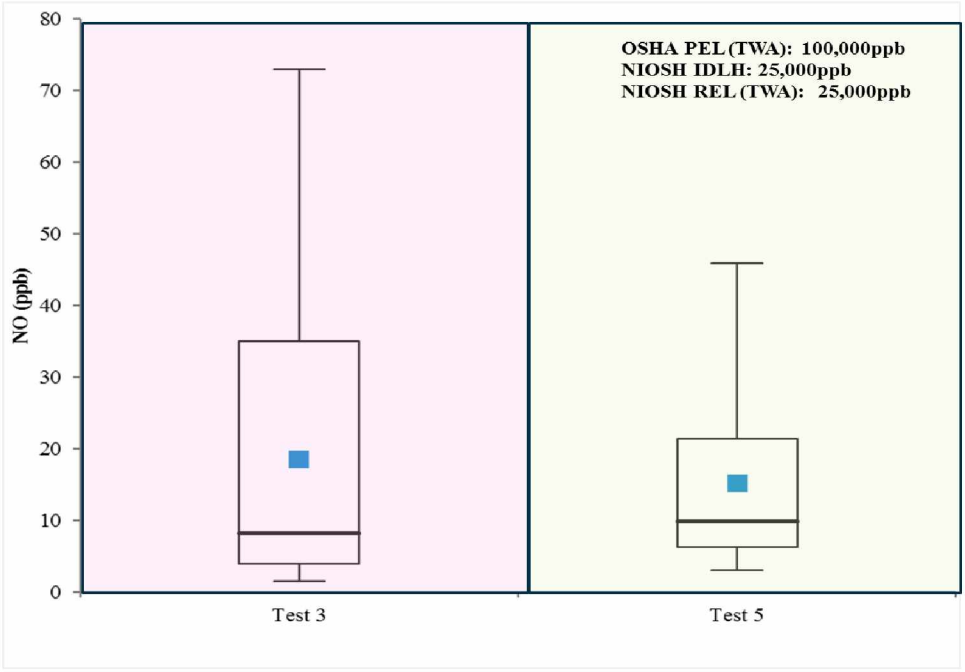

Figure 18 **Box plots showing measured NO concentrations during burns, in comparison to established exposure limits and air quality standards. Average concentrations marked with a blue square.**

Figure 19 below contains NO_2 data, shown with 15 sec intervals, collected during Tests 2, 3, and 5. Two different instruments were used for sample collection, with the one utilized for Test 2 only being capable of logging concentrations in the ppm range. The maximum measured NO_2 concentrations during Test 3 and Test 5 were 246 ppb and 329 ppb, respectively. The average maximum concentration measured for the three tests was 287.5 ± 41.5 ppb. The average concentration measured during the three burns was 81.1 ± 16.9 ppb. Figure 20 contains NO_2 concentrations measured during Tests 2, 3, and 5, with data presented as boxplots, and compared to applicable exposure limits. The blue square of the plots represents the average concentration for each test.

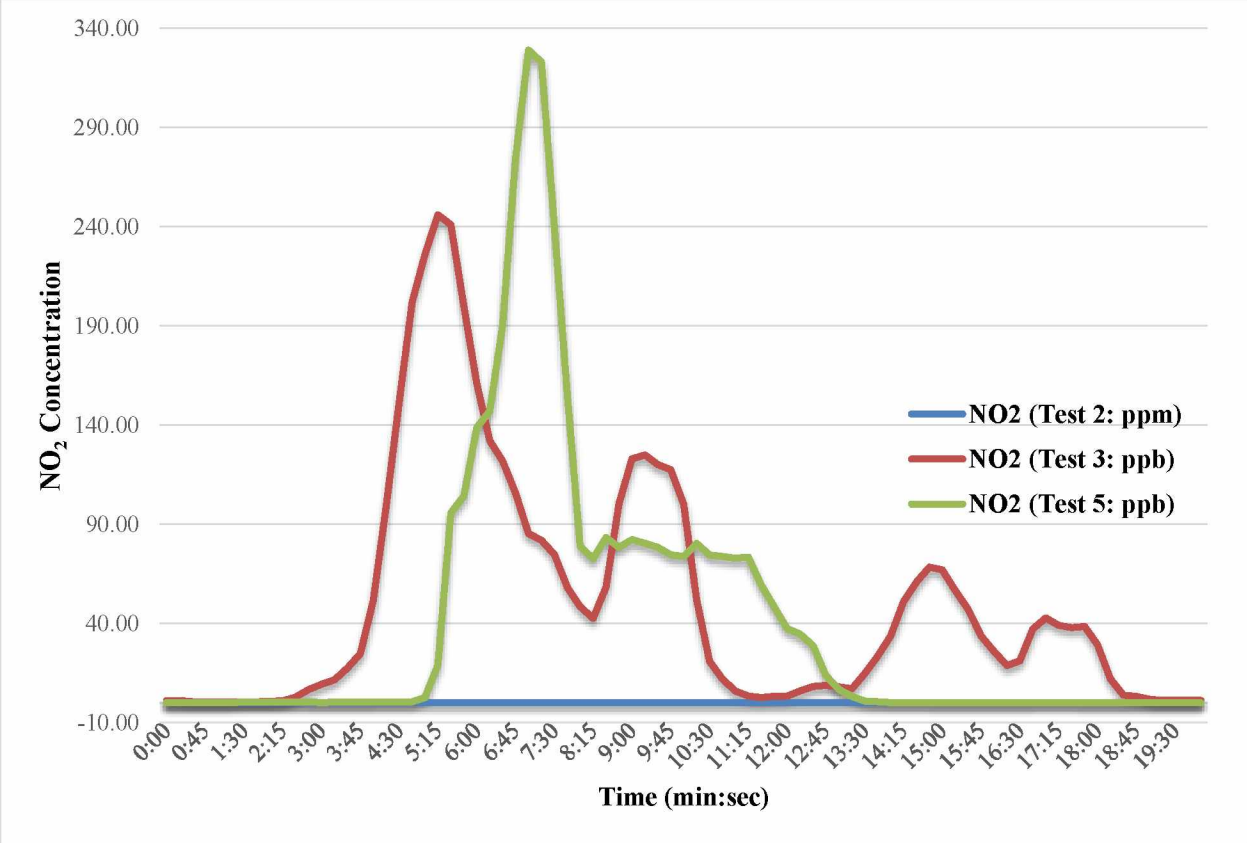

Figure 19 **NO_2 concentrations measured during Test 2, 3, & 5, depicted at a 15sec interval.**

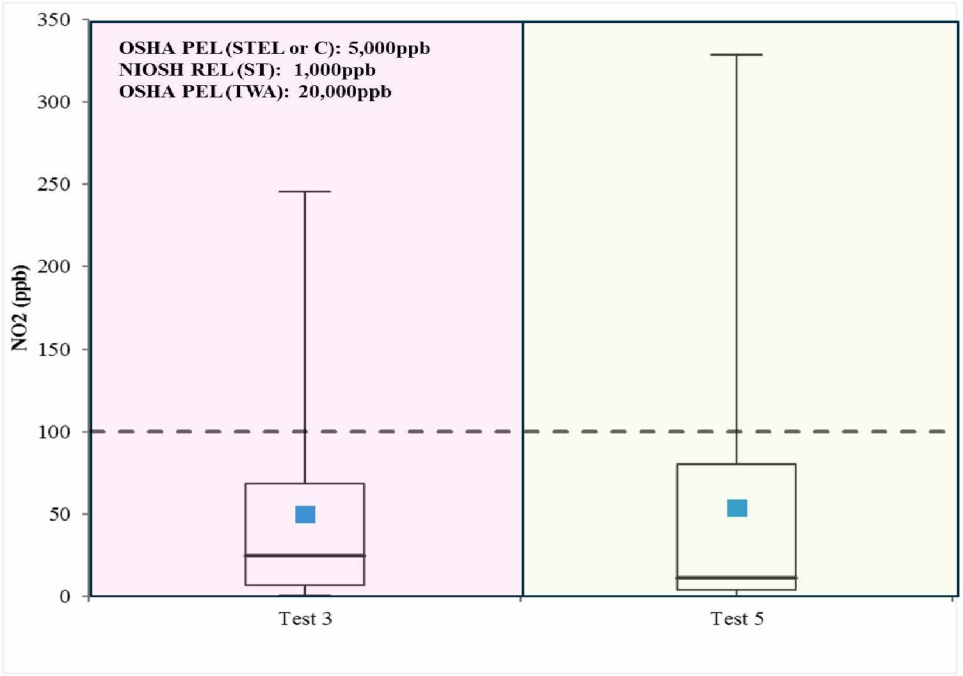

Figure 20 **Box plots, with average concentrations marked with a blue square, showing measured NO_2 concentrations during burns, in comparison to established exposure limits and air quality standards.**

Figure 21 below contains NO_x data, shown with 15sec intervals, collected during Tests 2, 3, and 5. Two different instruments were used for sample collection, with the one utilized for Test 2 only being capable of logging concentrations in the ppm range. The maximum measured NO_x concentrations during Test 3, and Test 5 were 319 ppb and 375 ppb, respectively. The average maximum concentration measured for the three tests was 347.0 ± 28.0 ppb. The average concentration measured during the three burns was 101.6 ± 12.0 ppb. Figure 22 contains NO_x concentrations measured during Tests 2, 3, and 5, with data presented as boxplots. The blue square of the plots represents the average concentration for each test.

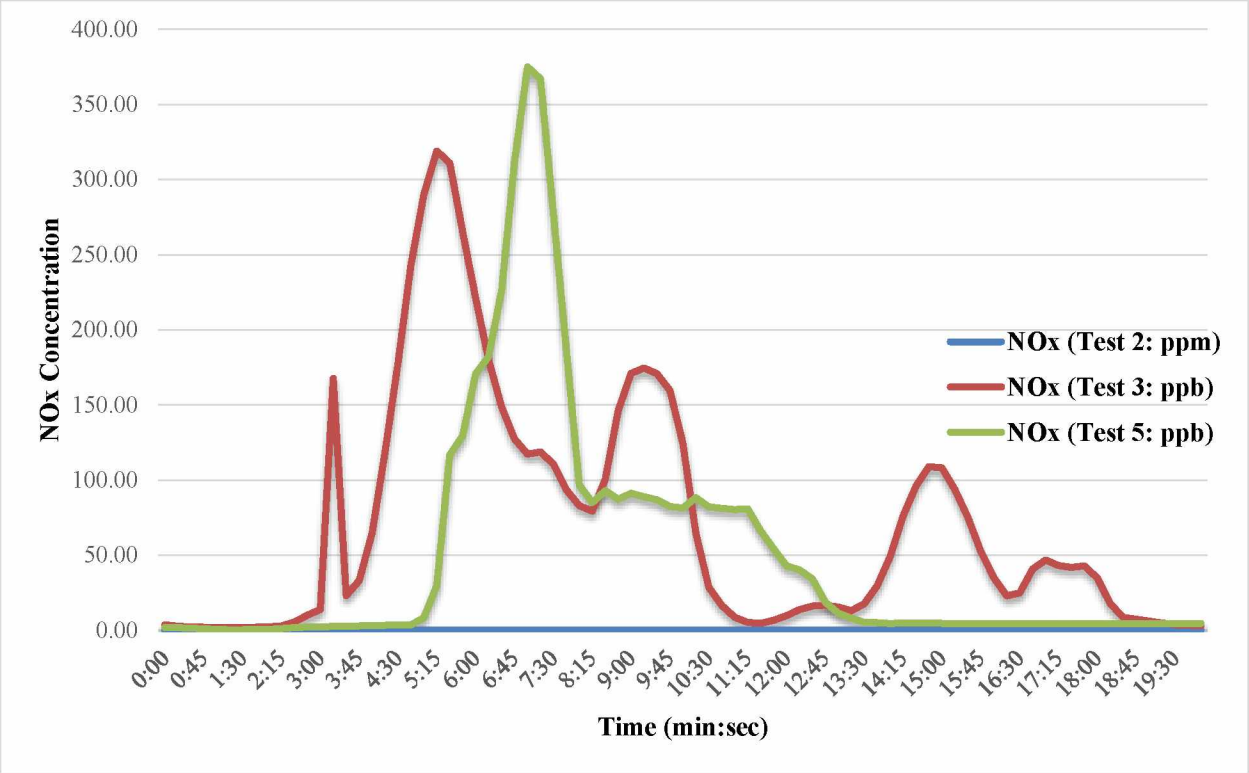

Figure 21 **NO_x concentrations measured during Test 2, 3, & 5, depicted at a 15sec interval.**

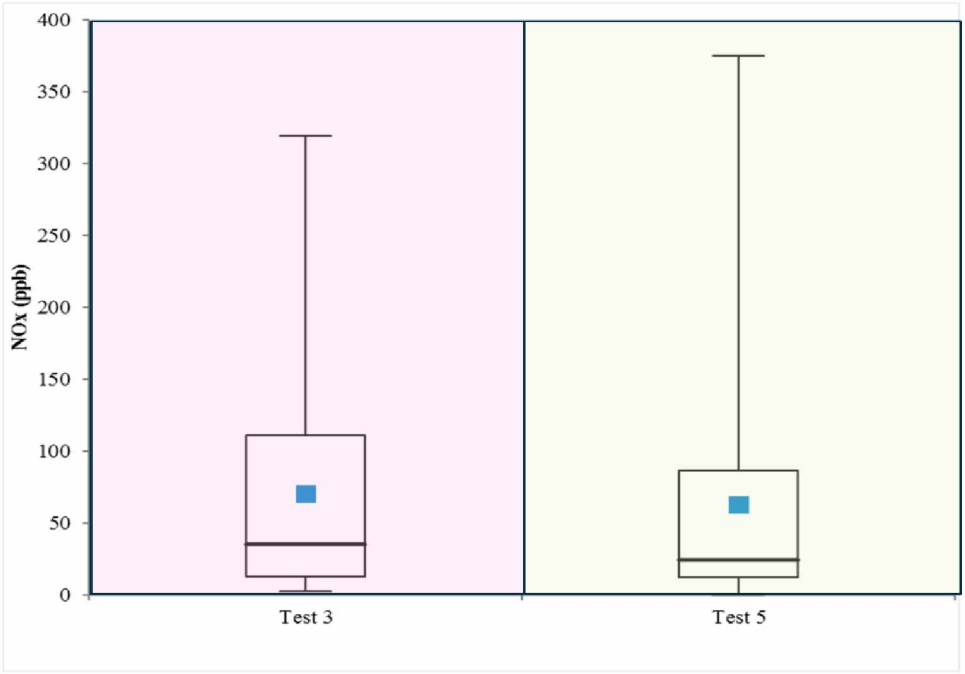

Figure 22 **Box plots are showing measured NO_x concentrations during burns. Average concentration is marked with a blue square.**

Figure 23 below contains Total VOC data, shown with 15sec intervals, collected during Tests 2, 3, and 5. The maximum measured Total VOC concentrations during Test 2, Test 3, and Test 5 were 27.2 ppm, 18.8 ppm, and 6.2 ppm, respectively. The average maximum concentration measured for the three tests was 17.4 ± 8.6 ppm. The average concentration measured during the three burns was 2.1 ± 1.3 ppm. Figure 24 contains Total VOC concentrations measured during Tests 2, 3, and 5, with data presented as boxplots. The blue square of the plots represents the average concentration for each test. It should be noted that concentrations on the Y-axis are on a base-10 logarithmic scale with a constant (y+1) added to each data point.

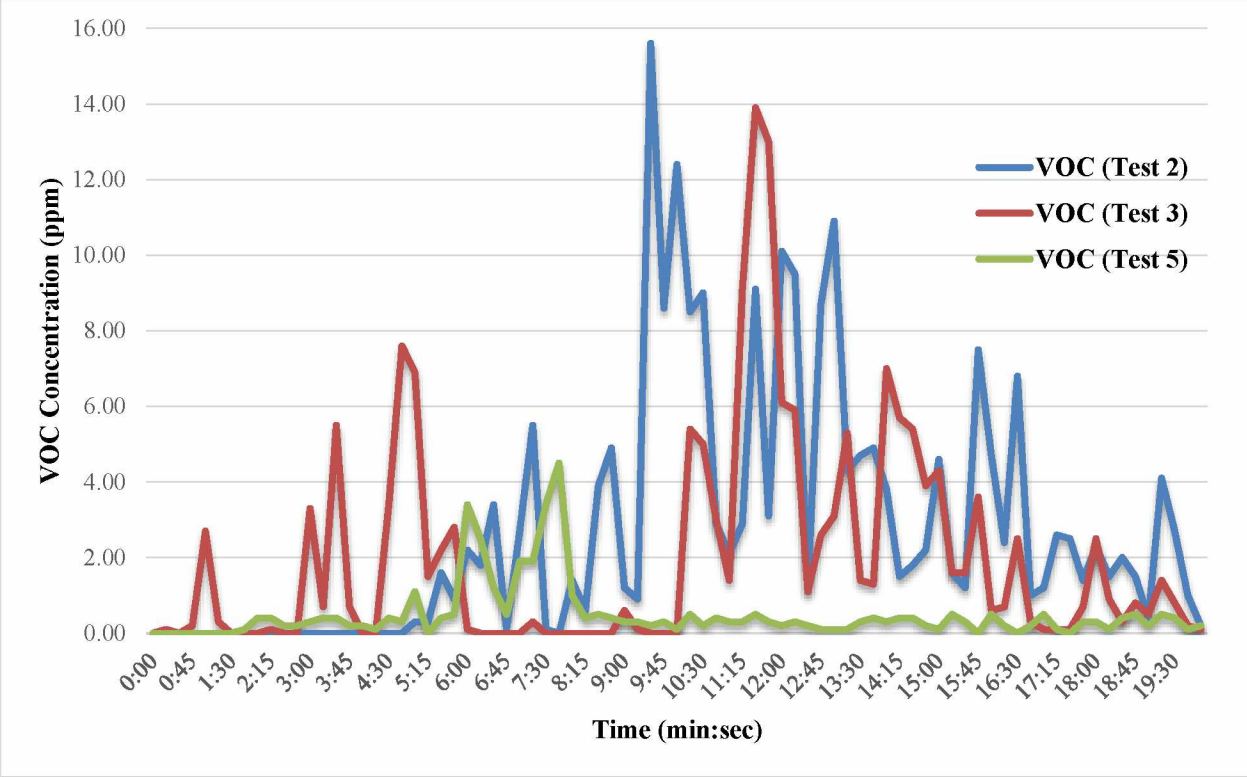

Figure 23 **VOC concentrations measured during Test 2, 3, & 5, depicted at a 15sec interval.**

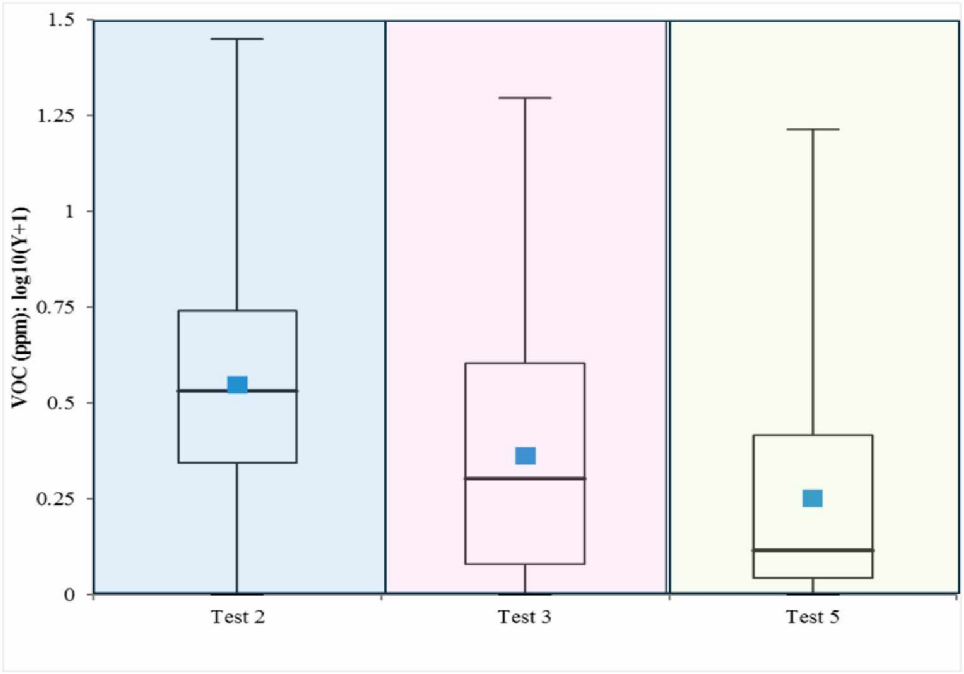

Figure 24 **Box plots, with average concentrations marked with a blue square, showing measured Total VOC concentrations during burns. Please note that concentrations on the Y-axis are on a base-10 logarithmic scale, with a constant (y+1) added to each data point.**

Table 5 provides information on mean maximum concentrations of the various combustion gasses and particulate matter sizes measured during Test 2, 3, and 5, as well as the calculated p-value and significance level. Table 6 compares the average concentration measured during Test 2, 3, and 5 to the applicable exposure limits and air quality standards. The data show CO, CO_2, SO_2, NO, and NO_2 concentrations significantly below OSHA TWA PELs, while PM-2.5 concentration (both mean maximum and average) was significantly above the OSHA STEL and NAAQS 24hr average. Furthermore, CO, CO_2, and NO concentration were significantly below NIOSH TWA RELs, while SO_2 concentration was significantly above the NIOSH TWA (mean maximum only) and NAAQS 1hr average (both mean maximum and average). Except for the PM-2.5 concentrations (both mean maximum and average) significantly above the NIOSH STEL, the concentration of all other compounds measured downwind, in the smoke plume was

significantly below the established STEL, ST, or C limits (both mean maximum and average). In addition, the mean maximum CO concentrations were significantly above the NAAQS 8hr allowed average. Cells of Table 5 & 6 stating that data is Not Available (N/A) is due to either an insufficient amount of data to conduct the statistical analysis or by the lack of established NIOSH or OSHA exposure limits.

Table 5 **P-values when comparing mean maximum concentrations with established exposure limits and air quality standards. Green equals significantly below, while red equals significantly above. NO_2 concentrations were above the NAAQS 1hr, but not significantly.**

Compound (unit measured)	Mean [Maximum] ± SD	OSHA PEL (TWA)	NIOSH REL (TWA)	OSHA PEL (STEL or C)	NIOSH REL (ST)	NIOSH IDLH	NAAQS (1hr)	NAAQS (8hr)	NAAQS (24hr)
CO (ppm)	20 ± 8	**2.44E-04**	**5.12E-03**	**3.67E-08**	**3.67E-08**	**3.04E-12**	**5.12E-03**	**1.61E-02**	*N/A*
CO_2 (ppm)	1785 ± 711	**8.10E-05**	**8.10E-05**	**1.72E-09**	**1.72E-09**	**3.78E-10**	*N/A*	*N/A*	*N/A*
PM-2.5 (mg/m^3)	204.26 ± 2.04	*N/A*	*N/A*	**3.26E-03**	*N/A*	*N/A*	*N/A*	*N/A*	**3.18E-03**
SO_2 (ppm)	3.4 ± 1.1	**1.25E-02**	**1.83E-02**	**1.25E-02**	**1.25E-02**	**3.54E-11**	**5.68E-04**	*N/A*	*N/A*
NO (ppb)	60 ± 14	**1.72E-04**	**1.72E-04**	*N/A*	*N/A*	**4.30E-05**	*N/A*	*N/A*	*N/A*
NO_2 (ppb)	288 ± 42	*N/A*	*N/A*	**2.80E-03**	**1.85E-02**	**6.70E-04**	**6.93E-02**	*N/A*	*N/A*
NO_x (ppb)	347 ± 28	*N/A*	*N/A*	*N/A*	*N/A*	*N/A*	*N/A*	*N/A*	*N/A*
VOCs (ppm)	17.4 ± 8.6	*N/A*	*N/A*	*N/A*	*N/A*	*N/A*	*N/A*	*N/A*	*N/A*

Table 6 **P-values when comparing mean average concentrations during the burns with established exposure limits and air quality standards. Green equals significantly below, while red equals significantly above.**

Compound (unit measured)	[Average] ± SD	OSHA PEL (TWA)	NIOSH REL (TWA)	OSHA PEL (STEL or C)	NIOSH REL (ST)	NIOSH IDLH	NAAQS (1hr)	NAAQS (8hr)	NAAQS (24hr)
CO (ppm)	4 ± 5	**0.00E +00**	**0.00E +00**	**0.00E +00**	**0.00E +00**	**0.00E +00**	**0.00E +00**	**0.00E +00**	*N/A*
CO_2 (ppm)	526 ± 193	**0.00E +00**	**0.00E +00**	**0.00E +00**	**0.00E +00**	**0.00E +00**	*N/A*	*N/A*	*N/A*
PM-2.5 (mg/m^3)	8.72 ± 22.25	*N/A*	*N/A*	**5.59E -09**	*N/A*	*N/A*	*N/A*	*N/A*	**7.49E -40**
SO_2 (ppm)	0.4 ± 0.7	**0.00E +00**	**0.00E +00**	**0.00E +00**	**0.00E +00**	**0.00E +00**	**5.28E -200**	*N/A*	*N/A*
NO (ppb)	17 ± 16	**0.00E +00**	**0.00E +00**	*N/A*	*N/A*	**0.00E +00**	*N/A*	*N/A*	*N/A*
NO_2 (ppb)	51 ± 72	*N/A*	*N/A*	**1.86E -299**	**1.99E -183**	**0.00E +00**	**8.02E -15**	*N/A*	*N/A*
NO_x (ppb)	66 ± 83	*N/A*	*N/A*	*N/A*	*N/A*	*N/A*	*N/A*	*N/A*	*N/A*
VOCs (ppm)	2.3 ± 3.1	*N/A*	*N/A*	*N/A*	*N/A*	*N/A*	*N/A*	*N/A*	*N/A*

Results achieved during the tests are in agreement with previous studies and guidance documents (Buist et al., 2013a; Fingas, 2010a; Fingas, 2013; Fingas, 2014a; Fingas, 2014b), which state that particulate matter is the main concern when conducting an in-situ burn of crude oil. It should be noted that for this study, the particulate matter concentrations recorded were outside of the measurement range of the instrument, which is 100 mg/m^3, according to the manufacturer (TSI Incorporated, 2010). For the data collected during the burn period of Test 3, 2% of the logged data (10 of 546 data points) was above 100 mg/m^3; while only 1% (7 of 685 data points) was above the 100 mg/m^3 for Test 5. When excluding any concentrations above 100 mg/m^3, the average PM-2.5 concentration for Test 3 and Test 5 was 7.83±17.11 mg/m^3 and 6.10±13.81 mg/m^3, respectively. The maximum PM-2.5 concentration for each burn, when

excluding any logged data above 100 mg/m^3, was 99.77±17.11 mg/m^3 for Test 3 and 81.72±13.81 mg/m^3 for Test 5. When combining data from both burns, and excluding any data points above 100 mg/m^3, the average PM-2.5 concentration was 6.86±15.38 mg/m^3 and the average maximum concentration was 90.74±9.02 mg/m^3. Even though both the average and maximum concentrations are below the original dataset when excluding all data points above 100 mg/m^3, the concentrations are still significantly (P<0.01) above OSHA STEL as well as the NAAQS 24hr average (Figure 25).

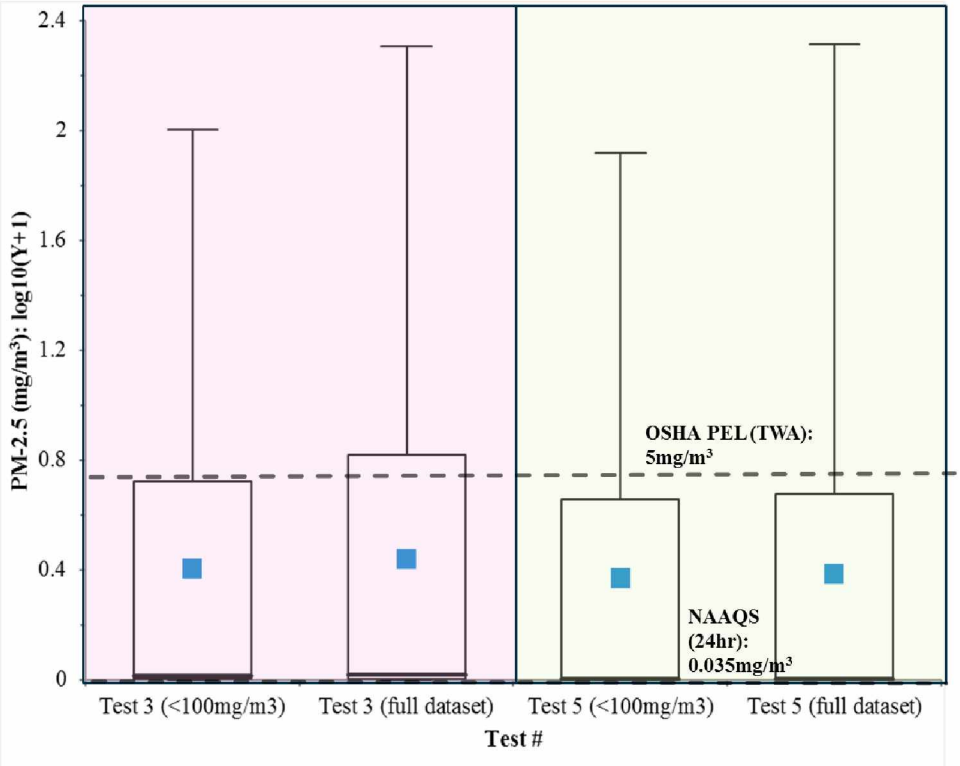

Figure 25 **Box plots are showing measured PM-2.5 concentrations during burns, with and without data points above 100 mg/m^3, in comparison to established exposure limits and air quality standards. Average concentrations are marked with a blue square. Concentrations on the Y-axis is on a base-10 logarithmic scale, with a constant (y+1) added to each data point.**

As noted by Fingas (2014a), the data collected in this study is subject to various environmental factors causing large variances in the logged data. Even when averaging 15 seconds of data to create one data point, the "noise" or "jaggedness" depicted in the various line charts of this section remained. This finding can likely be contributed to changes in wind speed and direction that moved the smoke plume away from the instruments in both the horizontal and/or vertical direction. Although partially or largely explained by those elements, it is hard to get a clear and complete picture of the various combustion gas and particulate matter concentrations emitted during a field scale experiment in an uncontrolled environment similar to what would be conducted and experienced during a real spill event.

Other major findings include the high levels of all combustion gasses measured during this study. No previous studies have measured SO_2 concentrations above 2 ppm while this study had an average maximum measured concentration of 3.4±1.1 ppm over the three burns, which is significantly above the NIOSH TWA REL. It should be noted, however, that NIOSH's TWA indicates a time-weighted average concentration for up to a 10-hour workday during a 40-hour workweek, and that the average concentration of SO_2 during the burns was significantly below the established exposure limit. Although measured concentrations for all other combustion gasses were significantly below established exposure limits, no studies found during the literature review had measured NO_x concentrations above 50 ppb; these tests produced data showing an average maximum concentration of 347±28 ppb and a mean average concentration during the burns of 102±12 ppb. Similarly, no studies could be found where the Total VOC concentration measured exceeded 1.1 ppm, while this study showed average maximum concentration at 17.4±8.6 ppm and a mean average concentration during the burns of 2.1±1.3 ppm. This finding could be considered inconclusive, however, because a portion of the VOCs

measured could have been emitted from the oil slick itself, located only 6 m from the instrument, and measured VOCs present within the smoke plume.

Overall, the significant concentrations recorded, and found to be higher than those reported in the prior studies, are likely due to a combination of factors: the study was conducted at a field scale (with a higher volume crude oil burned than many previous studies); also, there were fortunate wind conditions and placement of sampling instruments, which allowed for in and near-plume measurements of particulate matter and the various combustion gases. Although a few previous studies (Booher & Janke, 1997; Fingas et al., 1993; Fingas et al., 1996; Middlebrook et al., 2011; Gullett et al., 2016) utilized a larger volume of crude oil during their experiments, this study had a larger containment or basin to conduct the controlled burns in. That fact, in combination with the constant wind direction, is believed to have provided an unequaled opportunity to measure the maximum combustion gas and particulate matter concentrations emitted when burning the amount and type of crude oil utilized for this study. In addition, some of the findings during this study refute conclusions drawn by previous researchers such as Fingas et al. (1993) who stated that "direct-reading instruments do not detect the compound (SO_2) above background levels" and "CO and NO_x are not above the lower detection levels". Fingas (2014b) also noted that "sulphur dioxide, per se, is usually not detected at significant levels or sometimes not even at measurable levels" and that "the gas (CO) has only been measured when the burn appears to be inefficient, such as when water is sprayed into the fire". Finally, Fingas et al. (1999) also concluded that "carbon monoxide levels are usually at or below the lowest detection levels of the instruments", and that "sulphur dioxide is usually not detected at significant levels or sometimes not even at measurable levels". This study, and several others (Booher & Janke,

1997; Mulholland et al., 1996; Gullett et al. 2017), did, however, detect significant concentrations of CO, SO_2, and NO_x.

It was noted that, for the compounds where measurements were recorded during Test 2, 3, & 5, the concentrations were significantly higher during Test 2, when only 75 gal of crude oil was released, compared to Test 3 & 5 when 155 gal of crude oil was utilized. This is contrary to what one would believe since more than doubling the amount of crude oil was believed to lead to higher concentrations emitted. The reason for this finding is not known or completely understood, but we theorize that there is a correlation between the larger slick diameter during Test 2 compared to Test 3 & 5 (Table 2). If one were to assume that the entire slick during Test 2 was ignited at once, the oxygen demand would have been larger for that slick compared to the later tests, leading to both higher incomplete combustion gas concentrations. Another reason for this finding could be that the larger slick diameter during Test 2 led to a continuous "feed" of unignited crude oil into the west corner of the basin (Figure 5), which allowed for a more vigorous combustion process and higher concentrations of complete combustion. This theory would, however, not explain the higher levels of CO present. The observation or finding could also be the result of more favorable winds during Test 2, carrying the emissions straight toward the sampling station and allowing for the instrument to record the higher concentrations.

Concentrations measured for CO and CO_2 are similar to those found by Mulholland et al. (1996) and Booher & Janke (1997) but differ from the findings of the other studies reviewed. Similarities in findings can likely be contributed to the similarities in experimental setup; all three studies collected measurements from within the visible smoke-plume and from less than 10 m away from the source. Consequently, the emitted CO and CO_2 did not have an opportunity to diffuse, which is likely the mechanism that leads to the lower concentrations found in other

studies. During this study, the ratio of CO_2 to CO was found to be highest during Test 5 where the average ratio during the burn was 465:2 and 475:1 for the instrument (Q-Trak) #1 and #2, respectively. During Test 2 and Test 3, the average CO_2:CO ratio during the burns was 619:7 & 86:1 (Q-Trak #1 & #2) and 496:5 & 516:5 (Q-Trak #1 & #2), respectively. Tying these results back to the last paragraph, the finding that average particulate matter and combustion gas concentrations during Test 2 were higher than Test 3 & 5 could be explained by a more oxygen starved or incomplete combustion process. It should be noted that background CO concentrations were above expected (1-2 ppm) during Test 2 & 3, but were after recalibration back to 0 ppm during Test 5. Compared to previous studies, where measured CO_2 to CO ratios have ranged from 50:1 (Mulholland et al., 1996) to 109:1 (Gullett et al., 2017), the results from Test 2 & 3 show similar ratios, while the Test 5 ratios are significantly ($P<0.01$) above.

As mentioned previously, the results from this study agree with previous findings that particulate matter is the main compound of concern, particularly for the general public and wildlife. Responders located in closer proximity to the burn area should be made aware, however, that even combustion gas concentrations can exceed established exposure limits, which would require them to use additional personal protective equipment (PPE). In addition to PPE, responders should receive the training required to conduct the operation safely and should have the knowledge to be aware of potentially hazardous situations or environments. Monitoring of the responders' work environment should be conducted as needed to ensure that occupational standards such as OSHA's PELs and NIOSH's REL are not violated.

3.2 Results and Discussion Related to Herder Analysis

Chromatograms similar to Figure 26 were obtained when analyzing pure Siltech OP-40, showing the presence of the herding agent functional group eluted between 14 and 24 min (Billings et al., 2016). The used internal standard, D-5 nitro-benzene, is detected after approximately 8 minutes, while the OP-40 functional group (octamethyltrisiloxane; Figure 27) with a mass-to-charge ratio (m/z) of 191, 207, and 221 used for quantitative calculations is detected between 14 and 25 min (Billings et al., 2016). When analyzing the carbon disulfide and potential OP-40 herding agent mixture, there were no functional groups with the 191, 207, and 221 m/z ratio within the detectable range of the instrument.

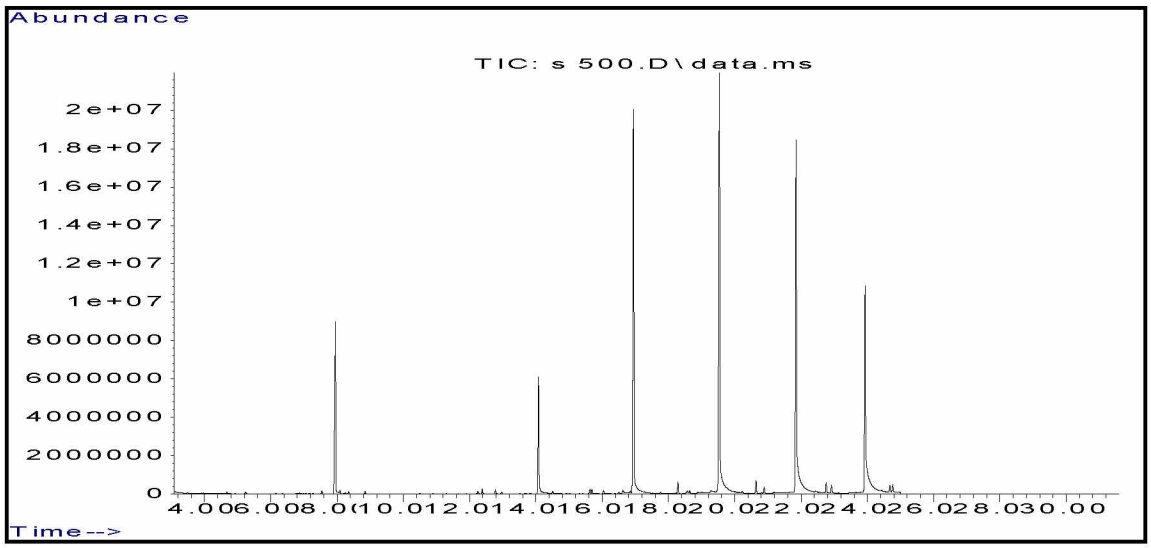

Figure 26 Chromatogram obtained when analyzing pure Siltech OP-40, showing the presence of the herding agent functional group between 14 and 25 min.

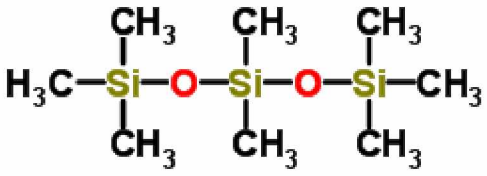

Figure 27 Chemical structure of octamethyltrisiloxane ($C_8H_{24}O$).

No studies have been published related to herding agent emissions during crude oil ISBs, but the functional groups of neither Thickslick 6535 nor Siltech OP-40 are expected to be emitted through the smoke plume due to lack of heat transfer from the flames to the water surface. This study only involved the potential emission of Siltech OP-40, and the results can be explained by the herding agent's high boiling point that would prevent it from going through a liquid-to-gas phase change during the combustion process. The GC/MS analysis conducted as part of this study required a GC injection port temperature of approximately 300°C before the Siltech OP-40 vaporized sufficiently for the MS to be within a 10 % margin of error when analyzing known concentrations of the herding agent. Buist et al. (1999) report that only 1-to-3 % of the 900-to-1200°C flame temperatures during an ISB would radiate back to the water or slick surface. The herding agent is, therefore, more likely to remain either on the water surface or bound to the crude oil residue. Methods will need to be refined when detecting herding agent in the airborne plume, as the high concentrations during the field scale burns conducted on April 22-27, 2015 caused the flow meters to malfunction. One proposed method is to filter out some of the particulate matter emitted during the crude oil combustion process, would be to use larger diameter sorbents tubes with more activated carbon and space for the particulate matter. Another method to consider is the use of vacuum canisters, now available in 400 ml size and capable of flow rates up to 340 mL/min that allow for sampling times as low as five seconds to meet QA/QC requirements (SGS, 2017).

3.3 Results and Discussion Related to Wind Analysis

The analysis of wind speed in correlation with combustion gas concentrations was deemed inconclusive due to concerns of data unreliability. The Met One E-BAM at monitoring

station #1 had been moved from the original location to make room for passing equipment, and was never repositioned on a level surface nor recalibrated. Wind data was recorded and is shown in Figures 28 & 29, but the consistency in wind direction does not mirror the observed on-site wind direction that showed larger variance. After reviewing photos from the test dates, it was concluded that the device was repositioned on an uneven surface, which caused the weighted tip of the wind direction arrow to remain stagnant in the north northwest direction. Both the wind speed and direction sensors are joined as one unit, and the wind speed data was therefore also deemed unreliable since is also would have been pointed downwards. The Campbell Scientific CR1000 data logger with the RM Young 05103 Wind Monitor was found to only log data every 15 min, and none of those data points coincided with a burn event.

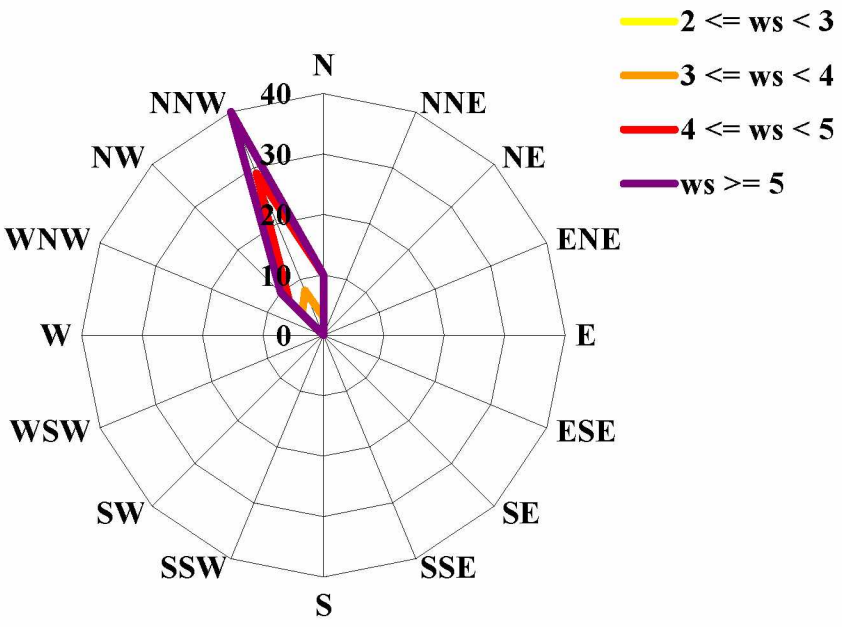

Figure 28 **Wind rose created with logged wind speed and direction from the Met One E-BAM located at wind monitoring station #1.**

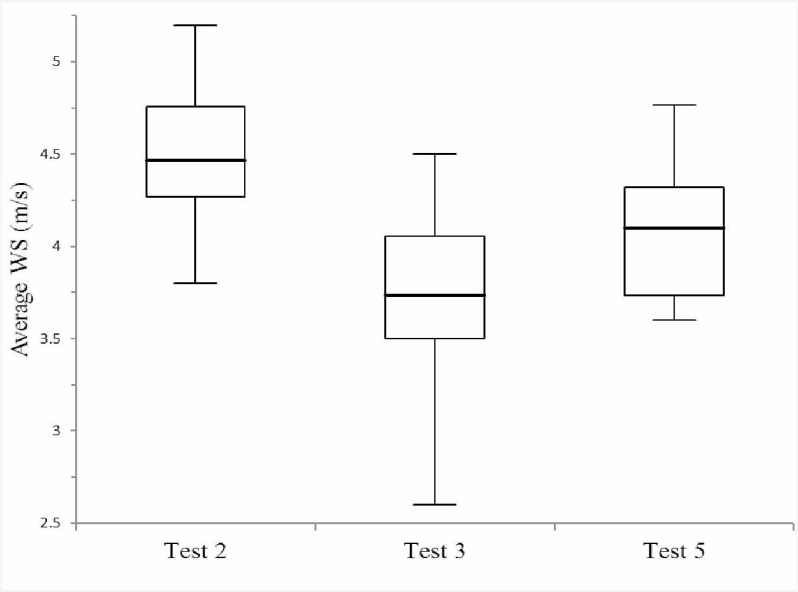

Figure 29 **Box plots showing average wind speed (m/s) during Test 2, 3, & 5, logged by the Met One E-BAM located at wind monitoring station #1.**

4 Conclusion and Future Research

The emissions of particulate matter and various combustion gasses is of significance when conducting an in-situ burn, and some emitted compounds can pose an imminent and substantial threat to human health and welfare. Particulate matter, SO_2, and CO concentrations were found to be significantly ($P<0.01$) above established exposure limits and/or air quality standards and should be taken into consideration when assessing potential risks from an in-situ burn to responders and the general public. This study utilized herding agents as a way to contract and thicken the released crude oil slick, but no volatilized silicone based functional groups were found to be present in the emitted smoke plume. To our knowledge, this was the first study to address this question as well as measure gaseous emissions from herding agent-mediated in-situ crude oil burns and focusing on concentrations of particulate matter and various combustion gasses close to the burn site where response personnel could be at risk.

Future research to be conducted should include a scalability study in a controlled environment, where projected concentrations of particulate matter and various combustion gases, established by previous studies (Fingas, 2010a; Fingas et al., 1993; Fingas et al., 1994; Fingas et al., 1995; Ross et al., 1996) and available plume trajectory models such as ALOFT-FT (A Large Outdoor Fire plume Trajectory-FT; McGrattan et al., 1997), should be validated to confirm that hypothesized concentrations of the various combustion by-products are accurate and predictable. In addition to confirming scalability, there is a need to test emissions from ISBs with systematically varied oil type/composition, weathering state of oil, percentage ice-coverage, and other environmental conditions such as temperature and wind speed. There are many sporadic studies, but most of the research has focused on the feasibility of conducting ISBs. The few published researchers focusing on presence/absence of emitted compounds, although some have

attempted to measure concentrations emitted with varying results. A systematic pilot scale study would shed additional light into the driving factors of emission concentrations during an ISB. As a follow-up, a similar study could be conducted where a herding agent mitigated burn is studied to clarify any potential concerns regarding reduced burn efficiency due to over-application of the herder. Due to the composition of the herding agent available to the author, Siltech OP-40 (a silicon based product), and the small amount expected to be applied for adequate slick thickness, no significant effect to projected emissions is expected.

Particulate matter is the main concern when conducting an in-situ burn of crude oil. Therefore the potential to reduce the concentration is intriguing and should be researched until a cost-effective alternative is discovered. The discoveries by Demirel and Barsan (2016) are promising and should be researched further. Unfortunately, an agent such as Ecopomex™ might not be as applicable for the Arctic and especially not during pack ice conditions, as additional recovery of the remaining solids containing crude oil might not be possible, even after a burn. On the other hand, any reduction in contaminants on top of the water is a positive effect, but the net environmental benefit comparing the decrease in particulate matter concentration and reduced burn efficiency needs to be evaluated.

The current "In Situ Burning Guidelines for Alaska" (ADEC et al., 2008) does not include any specific information or guidelines for response operations in the Arctic environment, and no information regarding burns in conjunction with herding agents or ice-infested waters is available. It would be of benefit for the regulatory agencies to prepare a burn plan specific for the Arctic before an incident occurs. This would allow the industry to load templates of the burn specific plans and forms into their Incident Management Software, and the lag time between

deciding that mechanical or other non-mechanical response tactics are impractical to initiating a burn will be minimized.

Finally, I believe the spill response community, or at least the individuals contributing to the current body of knowledge, need to come together to establish data gaps, settle on conflicting data that has been published, requirements for how and where data should be collected, and establish a peer-review process for guidance documents. Although a real spill event would never occur in a controlled environment, the state of knowledge for emissions during large-scale in-situ burns could benefit from a study conducted in such a setting. Currently, the available data is contradictory, primarily because researchers use methods and interpret the results at their discretion and then publish data that has not been peer-reviewed. For example, if weather conditions did not allow for a researcher to collect data within an area of the plume where certain emitted compounds are present during a burn, the conclusion from that study should not be that the compounds are not present at all or of concern. I believe this issue stems largely from the fact that only a small number of individuals are conducting research related to oil spill response. This leads a limited amount of available data that often seem somewhat biased, depending on the entity publishing the document. A process to filter out some of the obsolescent references, by for example creating a database for ISB related papers where up-to-date literature can be stored, could be of benefit to the response community.

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